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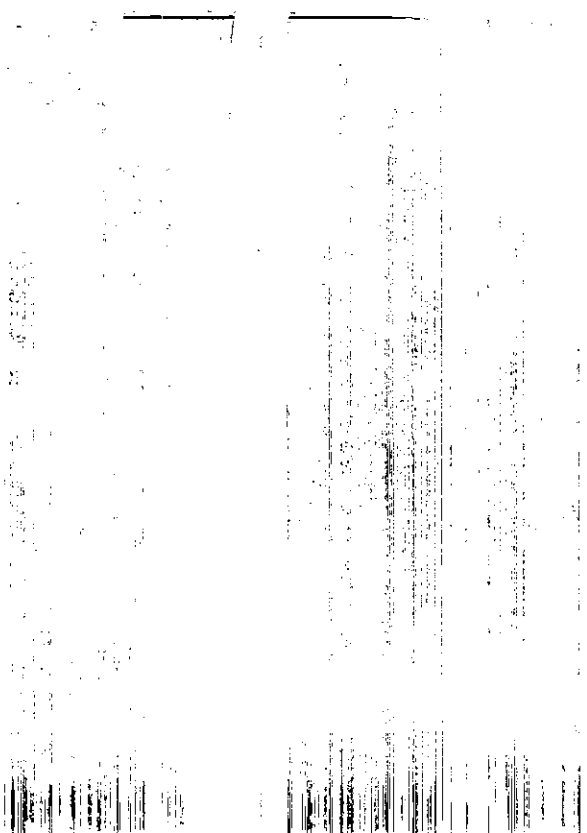

TRANSITION METAL COMPLEXES OF ETHANOLAMINE

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Walter Jack Howard

In Partial Fulfillment

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TRANSITION METAL COMPLEXES OF ETHANOLAMINE

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SUMMARY

The preparation, magnetic properties, and spectral properties of several transition metal complexes of ethanolamine have been investigated. In addition, crystal and molecular structures have been investigated for a dinuclear complex of ethanolamine.

This thesis reports a new preparation for the compound $Co(OC_2H_4NH_2)_3 \cdot 3H_2O$ starting with a cobalt(III) starting material. The material prepared was then used as a building block to prepare several trinuclear complexes of the general formula $M'[Co(OC_2H_4NH_2)_3]_2X_2 \cdot NH_2O$ where M' may be one of several transition metals. Compounds were prepared where M' was Co(II), Zn(II), Ni(II), Mg(II), and Cu(II). Magnetic properties were used to determine that the cobalt in the starting material $Co(OC_2H_4NH_2)_3 \cdot 3H_2O$ was actually a cobalt(III) ion as evidenced by a magnetic moment of zero Bohr Magnetons. Magnetic studies were also used to determine that, in the trinuclear complex with Mg(II) as the central ion, there was approximately two percent of the cobalt(II) present as the central atom.

The preparation, crystal structure, and molecular structure investigations for a dinuclear complex, $Ni(OH_2C_4H_4NH_2)_3Co(OC_2H_4NH_2)I_2$, are also reported. The actual mechanism of the formation of this complex is not clear since no free ethanolamine was present during the preparation. The structure consists of the tris-chelate octahedra bonded by very strong face-to-face hydrogen bonding between the oxygens. The bond distance between oxygens here is 2.5 Å while the shortest hydrogen bond reported is

2.41 Å. The ethanolamine rings exhibit a disorder in the nitrogen and oxygen positions which was resolved. When the two possible ring orientations were resolved and compared to a unit of the type $Co_3(OC_2H_4NH_2)_6^{2+}$, it was seen that one of the disordered units corresponded quite well to the distances in the trinuclear complex while the other possible unit was somewhat different. The results indicate that the species present must actually be a Ni-Co dimer and not a mixture of Ni-Ni, Co-Co, and Ni-Co dimers.

A partial structure of the compound $Co_3(OC_2H_4NH_2)_6I_2 \cdot 6H_2O$ indicated that the structure probably exhibited trigonal prismatic coordination around the central atom. This would mean that both of the trischelates of Co(III) were the same active isomers.

CHAPTER I

INTRODUCTION

Transition metal complexes with ethanolamine have been prepared previously but no thorough studies have been done on the resulting compounds. Almost no interest has been shown until very recently in polynuclear complexes with ethanolamine. The purposes of this work are: (1) to prepare dinuclear and trinuclear complexes of ethanolamine, (2) to study the resulting compounds in an attempt to determine crystal, molecular, and electronic structures, and (3) to study the properties of different isomers of the compounds.

Some of the earliest work in preparing transition metal complexes of ethanolamine was carried out by Hieber and Levy (1). Their work consisted mainly of syntheses and analyses with little study of the structures and properties of the resulting compounds. In this earliest work, Hieber and Levy worked only with cobalt. They prepared two types of complexes, one being a trinuclear complex and the other a dinuclear complex. Structures were proposed for each of these types of complexes. For the trinuclear complex, Figure 1 (please note that in this and in all other drawings a solid line —— is used to indicate the $-CH_2-CH_2-$ group and that hydrogens are shown only on the oxygen atoms necessary to make clear which ethanolamines are postulated as anions and which are postulated as neutral species), a linear arrangement of cobalts was predicted. Four of the oxygens were postulated to form single-atom bridges between cobalts with the other two positions on the central ion occupied by water molecules.

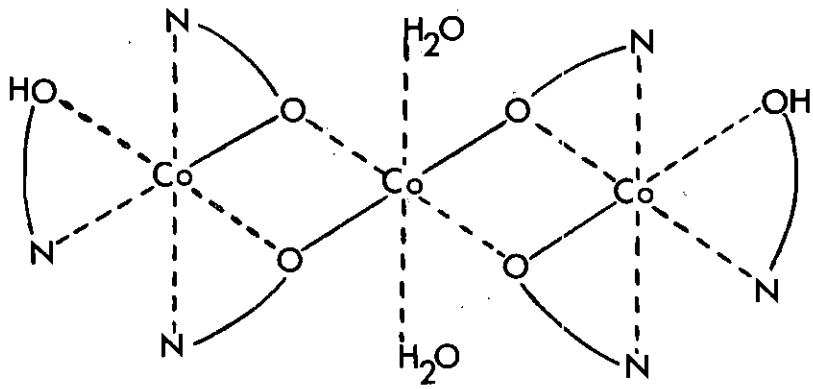

Figure 1. The Structure Proposed by Hieber and Levy for a Trinuclear Complex of Cobalt and Ethanolamine

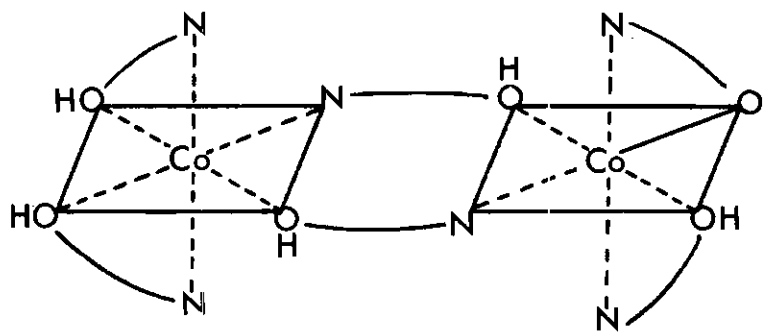

Figure 2. The Structure Proposed by Hieber and Levy for a Dinuclear Complex of Cobalt and Ethanolamine

The cobalts were all assumed to be cobalt(II). The structure for the dinuclear compound was postulated to be that shown in Figure 2. In this case the cobalts are in the +2 state but two of the ethanolamines are postulated as bridging the two cobalts.

Later Hieber and Levy (2) conducted a much more thorough attempt to prepare ethanolamine complexes with different metal ions. In their later work, they chose nickel(II), cobalt(II), copper(II), and zinc(II) as the metals to study. With cobalt(II) they were able to prepare a compound with a metal to ethanolamine ratio of 1:3. With the nickel(II) and copper(II) they were able to prepare compounds which had varying ratios of metal to ethanolamine. These reported ratios were 1:3, 1:2, and 1:1. With zinc(II) they were able to prepare compounds with ratios of 1:3 and 1:2 only.

Brintzinger and Hesse (3) carried out the next important work on ethanolamine complexes with cobalt(II) and chromium(III). With cobalt(II) they were able to prepare three different types of complexes. One of these was a tris-chelate of cobalt, $Co(ETA)_2(ETAH)\cdot 3H_2O$. (The abbreviation ETA will be used to indicate the anion of ethanolamine and the abbreviation ETAH will be used to indicate the neutral species.) This compound was postulated as containing cobalt(II). The second type of compound prepared was a dinuclear complex with the formula $Co_2(ETAH)_3(NO_3)_3$. This compound is analogous to the dinuclear compounds prepared previously by Hieber and Levy. A trinuclear compound of cobalt was also prepared and was postulated to be analogous to the trinuclear compound of Hieber and Levy even though the method of preparing the compound started with cobalt(III). Brintzinger and Hesse also tried to prepare complexes of ethanolamine with chromium(III). They succeeded in preparing a tris-chelate compound,

$Cr(ETA)(ETAH)_2Cl$.

Later studies by Yoneda and Kida (4) on some cobalt(III) complexes of ethanolamine yielded more information about possible structures for some of the dinuclear compounds. They used a cobalt(III) compound as the starting material and were able to prepare several dinuclear complexes with cobalt. They assumed that the compounds prepared contained cobalt(III) but they did not experimentally determine this. From the spectral studies of these dinuclear compounds they suggested two possible structures. One of these is shown in Figure 3 and involves face-to-face hydrogen bonding of the tris-chelate octahedra. Another possible structure suggested was corner-to-corner hydrogen bonding of two tris-chelate octahedra.

Work by Udovenko and co-workers (5) has added greatly to the understanding of ethanolamine complexes, especially those of cobalt. It has been shown in their work that the compounds prepared by Hieber and Levy and by Brintzinger and Hesse actually contained cobalt(III) and that Yoneda and Kida were correct when they assumed that the mononuclear and dinuclear compounds which they prepared contained cobalt(III). On the basis of this new information, a new structure was proposed for the trinuclear compound (Figure 4). A linear arrangement of the cobalts was still assumed, but all six oxygens form single-atom bridges linking the cobalts. These six oxygens were assumed to form an octahedron around the central cobalt. In addition to preparing several trinuclear complexes another tris-chelate was prepared. This compound was the pentahydrate $Co(ETA)_3 \cdot 5H_2O$ which had not been reported before.

Further work (6) resulted in the preparation of several dinuclear and trinuclear complexes with cobalt. The dinuclear complexes prepared

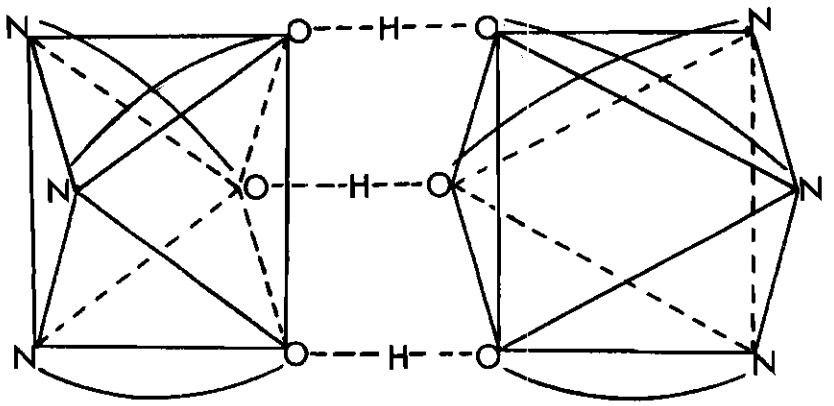

Figure 3. A Structure Proposed by Yoneda and Kida for a Dinuclear Complex of Cobalt and Ethanolamine

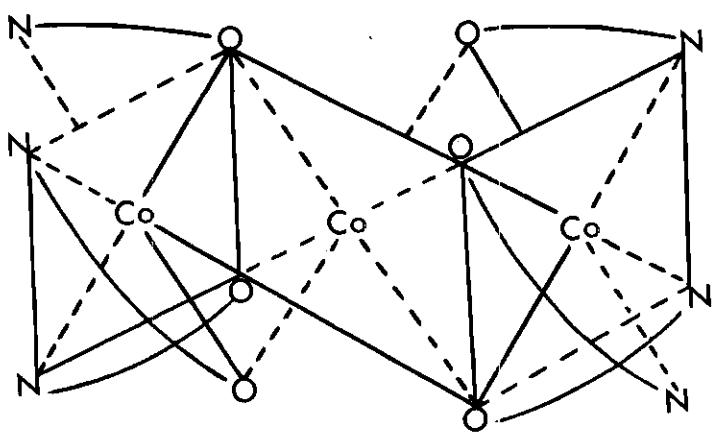

Figure 4. The Structure Proposed by Udovenko for a Trinuclear Complex of Cobalt with Ethanolamine

in this work were different from the compounds reported earlier. The general formula for these dinuclear species was $Co_2(ETA)_3(X)_2 \cdot n(H_2O)$. A different type of structure was predicted for these compounds and this structure is shown in Figure 5. In this structure, the oxygens all form single-atom bridges between the cobalts with water molecules occupying the vacant positions on the cobalt(II) ion. Here X is any halide ion.

It should be noted that if one has a complex involving the tris-chelate, there is the possibility of having different optical isomers. Fairly recent work by Brubaker and Douglas (7), who worked with a trinuclear complex of thio-ethanolamine (TETA), has shown that the two optical isomers and a meso form may be separated. The sulfur analog of ethanolamine could reasonably be expected to form compounds analogous to the ethanolamine complexes since sulfur is usually very similar to oxygen as far as compound formation and bonding. The work was conducted using a trinuclear complex in which all of the cobalts were in the +3 oxidation state $Co_3(TETA)_6Br_3$. The workers were successful in separating a d-d, an l-l, and a d-l or meso form of the material. The l-l and d-d forms would mean that the two tris-chelates were either both d forms or both l forms whereas the d-l form would contain one tris-chelate of each configuration.

It is also interesting to note that Udovenko and Stepanenko (8) have shown that geometric isomers of the compound $Co(ETA)_3 \cdot 3H_2O$ exist and that these isomers may be separated and studied. This work is very recent and up until this time, little thought was given to the possibility of cis and trans isomers. In the majority of the structures postulated the tris-chelate was assumed to be cis. A trans isomer has been reported of the same composition as the cis isomer but with different spectral properties and

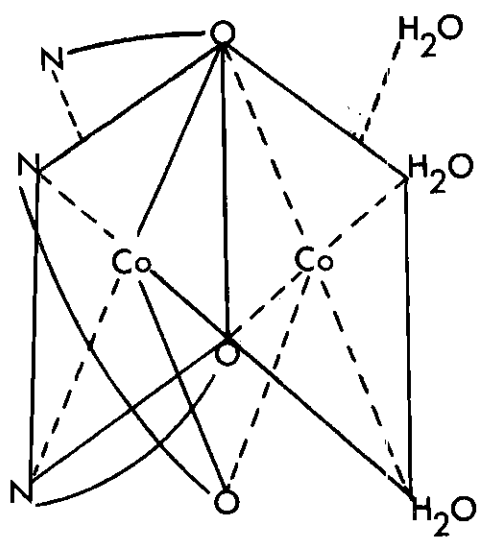

Figure 5. The Structure Proposed by Udovenko for a Dinuclear Complex of Cobalt with Ethanolamine

a different color. This possibility of a trans form of the tris-chelate raises many interesting questions concerning whether one actually has a cis or a trans form of the tris-chelate or a mixture of the two in a compound.

Recent work by Bertrand and Kelley (9) has provided impetus for the work discussed here. Their recent single crystal X-ray study of a trinuclear cobalt compound with ethanolamine has led to some interesting results. The compound studied was $Co_3(ETA)_6(Acetate)_2$. It was determined by analysis and magnetic studies that the material must contain one cobalt(II) ion and two cobalt(III) ions. X-ray structure determination revealed that the structure consists of a linear arrangement of cobalts with the six oxygens of the ethanolamines all acting as single-atom bridges between the cobalts.

The most interesting and unusual aspect of this compound was that the structure showed an almost perfect trigonal prismatic coordination around the central cobalt(II) ion. From the structure determination it was shown that the complex studied was an optically active isomer. The stability of the trigonal prismatic coordination over the regular octahedral coordination of cobalt was postulated as resulting from the interaction of the hydrogens on the methylenes of the ethanolamine groups. In the trigonal prismatic case the separation of the hydrogens is at a maximum. If this argument is correct and one looks at the models of the molecule, several interesting aspects of the structure become obvious. It may be seen that for a d-l isomer the most stable form of the molecule would be an octahedral arrangement of oxygens around the central metal atom.

One of the objectives of this work is to substantiate the argument

set forth above by preparing a d-l complex and doing single crystal X-ray studies of this compound.

Another interesting aspect of the chemistry of ethanolamine complexes involves heterometallic complexes. No work at all has been reported as far as preparing a heterometallic dinuclear compound but one would expect its existence since compounds analogous to the tris-chelate of cobalt have been prepared with other metals by Hieber and Levy and by Udovenko. Since these compounds do exist, it should be possible to prepare either heterometallic dinuclear or trinuclear compounds.

No work has been reported on preparing a heterometallic trinuclear compound with ethanolamine. A little work has been by Busch (10) in preparing some heterometallic complexes with thio-ethanolamine but little success has been reported.

It should be very interesting to prepare not only heterometallic dinuclear compounds but also heterometallic trinuclear compounds. Although the dinuclear compounds themselves would be interesting, the trinuclear species would hold the most interest. It would be very interesting to prepare a series of the trinuclear compounds which differ only in the identity of the central atom and then compare the properties of the series. Of interest should be the magnetic moments, the spectral properties, and X-ray structures.

The magnetic moments would serve as a test as to the identity of the metal ions present in some cases. If a trinuclear complex could be prepared which had a magnesium ion as the central atom, a check of the magnetic moment should tell if the magnesium were present since there should be no magnetic moment for a complex containing only magnesium and

cobalt(III). The magnetic moment for other trinuclear compounds would be informative but they would not tell conclusively the identity of the ions present in the compound.

The spectral properties of the trinuclear compounds should be very interesting. If one could prepare a trinuclear complex with some metal like magnesium as the central atom, it should be possible to study the spectra of other compounds and determine the contribution of the central ion to the spectra. The magnesium should have very little effect on the spectrum of the trinuclear species so that anything shown in the spectrum of this compound should be due to the terminal tris-chelates. This spectrum could then be subtracted from the spectra of other trinuclear complexes with different metal atoms at the center and the contribution of the central atom should be left. These spectra should also be related to the structures of the compounds as to whether they have octahedral or trigonal prismatic coordination around the central metal atom.

This work covers attempts first to prepare a homometallic trinuclear compound which is a d-l isomer and then other trinuclear complexes in which the central ion is different transitions metals and magnesium. A systematic attempt is made to prepare different compounds and then to study the properties of the compounds.

In the course of the work some dinuclear heterometallic compounds have been prepared and will be presented. The spectra of all of the compounds as well as the magnetic properties will be presented. Single crystal X-ray structure determination work has been completed on a heterometallic dinuclear complex and this structure will be presented and discussed.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes

$Co(ETA)_3 \cdot 3H_2O$

Since this compound was the basic building block for preparing both dinuclear and trinuclear complexes, it was very desirable to develop a method for producing the complex easily and in good yield. It was decided the best way to do this was to start with a cobalt(III) compound to produce the tris-chelate.

The salt used was $Na_3Co(CO)_3 \cdot 3H_2O$. The tris-chelate was produced by adding ethanolamine (0.06 mole) to the cobalt(III) salt (0.02 mole) in 5 ml of water. The resulting solution was heated moderately with constant stirring for about 20 minutes. The color of the solution changed from dark green to a reddish-purple. The solution on cooling gave fine purple needles. The resulting crystals were filtered with suction on a sintered glass funnel, washed twice with cold water and once with absolute ethanol and air dried.

Analysis:				
	Calc.	C = 24.57	H = 8.27	N = 14.33
	Exp.	C = 24.25	H = 8.42	N = 13.89

$MgCo_2(ETA)_6(Acetate)_2 \cdot 3H_2O$

In this preparation $Mg(Acetate)_2$ (0.001 mole) was dissolved in a solution of 50% ethanol and 50% methanol. Then the cobalt tris-chelate (0.003 mole) was added to the solution and the solution was then heated to about 60°C for about 25 minutes. The red precipitate which formed on

cooling overnight was filtered off and washed with ethanol and ether and then air dried. The yields from this method were not very good, so a better method was desired.

$MgCO_2(ETA)_6I_2 \cdot 3H_2O$

This compound was prepared like the acetate compound above except that a large excess of $Mg(Acetate)_2$ and a large amount of KI were added. The yield of this compound was much better than the acetate and produced crystals which were relatively pure.

Analysis:	Calc.	C = 17.78	H = 5.23	N = 10.37
	Exp.	C = 18.06	H = 5.84	N = 10.47

$CoCo_2(ETA)_6I_2 \cdot 6H_2O$

Method One. The first method is an exchange reaction which was carried out as follows. The compound $CoCo_2(ETA)_6Cl_2$ was prepared by a method previously reported (1), and then air dried. This material was judged pure enough to carry out the rest of the procedure. The iodide complex was prepared by dissolving the chloride compound in hot water and then adding potassium iodide to form a very concentrated solution. On cooling overnight red needle-like crystals formed. These crystals were filtered from the solution, washed with cold water and then ethanol and air dried. The crystals were recrystallized from water solution.

Analysis:	Calc.	C = 16.13	H = 4.75	N = 9.42	I = 28.41
	Exp.	C = 15.97	H = 5.30	N = 9.33	I = 28.92

Method Two. The complex was prepared directly from the tris-chelate by first dissolving $Co(NO_3)_2$ (0.001 mole) in hot water, then adding a large amount of potassium iodide, and then adding the tris-chelate (0.002 mole). The solution was then heated and stirred for one half hour, filtered while hot, and set aside to cool. The same type of crystals was produced

on standing for two days as with method one but the yield was not very good.

$NiCo_2(ETA)_6Br_2 \cdot 6H_2O$

Nickel bromide (0.012 mole) was dissolved in hot ethanol and about 5 ml of water. After heating this solution and stirring for a few minutes, the cobalt tris-chelate (0.02 mole) was added. The resulting solution was heated and stirred for about one half hour. The solution was filtered while hot to remove any unreacted material and set aside to cool. Square plate-like crystals that were dark red in color began to form immediately and after about two hours they were filtered from the solution and washed with an ethanol-water mixture (1:1). The crystals decomposed readily when exposed to air to form a red powder.

Analysis:					
	Calc.	C = 17.90	H = 6.02	N = 10.44	Ni = 8.42
	Exp.	C = 18.07	H = 6.26	N = 10.39	Ni = 8.36

$NiCo_2(ETA)_6I_2 \cdot 6H_2O$

Method One. Potassium iodide in large excess and nickel acetate (0.01 mole) were dissolved in water and heated moderately. The cobalt tris-chelate (0.02 mole) was added to this solution and the solution was heated and stirred for ½ hour. The solution was filtered while hot to remove any unreacted material and set aside to cool. Crystals of poor quality and very low yield were obtained.

Method Two. An alcoholic solution of $CoCl_2$ (0.04 mole) and $NiCl_2$ (0.02 mole) was prepared. This solution was slowly added to an alcoholic solution containing ethanolamine (0.12 mole). Potassium iodied was added in large excess to the solution and 5 ml of water was added to dissolve more of the potassium iodide. The solution was heated moderately and stirred for one half hour. The hot solution was filtered to remove any unreacted

material and set aside to cool. Hexagonal plate-like crystals formed which were filtered from the solution and washed with ethanol. The crystals were dried in vacuum and the weight loss was 11.3 percent which corresponds to six water molecules per formula unit.

Analysis:	Calc.	C = 16.00	H = 5.39	N = 9.35
	Exp.	C = 16.19	H = 5.08	N = 9.24

$Ni(ETAH)_3Co(ETA)_3I_2$

An alcoholic solution was prepared containing a 2:1 molar ratio of the tris-chelate of cobalt to $NiCl_2$. The solution was heated and stirred and potassium iodide was added in large excess. Enough water was added to make the solution about 9:1 ethanol to water. After heating for ½ hour the color of the solution changed from dark red to dark blue. The solution was filtered while hot and set aside. When the solution was evaporated to two-thirds the original volume, large approximately octahedral crystals formed. Further evaporation produced smaller almost perfect octahedral crystals. These crystals were filtered from the solution, washed with absolute ethanol, and air dried.

Analysis:	Calc.	C = 19.70	H = 4.96	N = 11.48	Ni = 8.02
	Exp.	C = 19.27	H = 5.41	N = 11.14	Ni = 8.06

$ZnCo_2(ETA)_6(Acetate)_2$

An alcoholic solution was prepared containing a 2:1 molar ratio of the tris-chelate of cobalt to $Zn(Acetate)_2$ and the resulting solution was heated with stirring for about an hour. The solution was set aside to cool and a red powder formed after several days. This material was filtered from the solution, washed with absolute ethanol, and air dried. The yield was very poor (enough for analysis only) and no crystals were ever obtained.

Analysis: Calc. C = 29.03 H = 6.40 N = 12.70
Exp. C = 29.69 H = 6.47 N = 12.33

Crystallographic Data and Structure Determination

Unit Cell Determination for $Ni(ETAH)_3Co(ETA)_3I_2$

An octahedral shaped crystal with triangular faces of approximately 0.2 mm was chosen for space group determination. The crystal was mounted on a glass fiber which was attached to a metal pin and then the metal pin was fastened to a goniometer head. After optically aligning the crystal as well as possible under a microscope, the goniometer was transferred to a Buerger precession camera. Precession photographs taken using nickel filtered copper Kα (λ = 1.5412 Å) radiation indicated that the crystal was cubic with a unit cell dimension of 13.60 ± 0.5 Å. The systematic absences h = 2n for the hk0 zone, l = 2n for the h0l zone and k = 2n for the 0kl zone uniquely determined the space group as Pa3 (No. 205) (11). The calculated density of 1.93 g/cm^3 for four formula units per unit cell agrees well with the observed density of 1.94 ± .02 g/cm^3 measured by the flotation method using a mixture of ethylene dibromide and carbon tetrachloride.

Solution of the Structure of $Ni(ETAH)_3Co(ETA)_3I_2$

The same crystal used for the space group determination was transferred to an automated Picker four-circle diffractometer. The alignment was performed following published instructions from the manufacturer (12). The four angles needed to define a reflection were determined for six reflections. Using these data, refined cell parameters and angles for the other reflections were determined by a least squares procedure (13). The cell parameters obtained were a = b = c = 13.600(7) Å, where the numbers in parentheses indicate the standard deviation of the last figure.

The X-ray intensity measurements were made on the same crystal as used for the unit cell determination except that Mo Kα (λ = 0.7107 Å) was used. The intensities were measured with a scintillation counter mounted 21 cm from the crystal. The intensities were collected by the θ - 2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1°/min. A symmetrical scan of 2° was taken about the calculated position for each reflection. When the scan was completed, stationary background counts of 20 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of the data. The threshold point was set so that the attenuators were inserted when the counting rate exceeded 10,000 counts/sec. The pulse height analyzer was set for approximately 90 percent window, centered on the molybdenum Kα peak. A recorder monitored the scan of each peak and the scans were examined for erratic background and the inclusion of Kβ peaks. A standard reflection (060) was intermittently scanned to check for crystal or instrument variations. No significant variation in the number of counts for this reflection was observed during the entire data collection period. Corrected intensities (CI) were obtained by subtracting three times the total measured background (since the time spent counting background, 40 seconds, was one third the time spent counting on the scan) from the integrated peak count (CT) by use of the following equation

$$CI = CT - (0.5(t_c/t_b)(bgd1 + bgd2))$$

where t_c is the scan time and t_b is the counting time of each background. The corrected intensities were assigned standard deviations according to

the formula (14)

$$\sigma(I) = (CT + 0.25(t_c/t_b)^2(bgd1 + bgd2) + (PI)^2)^{\frac{1}{2}}$$

where $\sigma(I)$ is the standard deviation of the i^{th} reflection and P is an "ignorance factor" which is used to keep very strong reflections from being weighted too heavily.

A total of 498 reflections was accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30 with P = 0.00. The intensities were corrected for Lorentz-polarization effects (15) but no corrections were made for absorption at this time.

Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer. The programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings (13), Zalkin's FORDAP fourier summation program (16), the Busing, Martin, and Levy ORFLS (17), XFLS (18), and ORFEE (19) programs, and a data reduction program by Kirkwood (20). In the structure factor calculations, the scattering factors tabulated by Ibers were employed for all atoms (21).

From a three-dimensional Patterson function (22), there was no evidence of atoms occupying fourfold positions, but two sets of eightfold positions were indicated. The eight iodides could be assigned to one of these sets and the four cobalt ions and the four nickel ions could be assigned to the other set. This implies a disordering of the two types of metal ions in one set of positions. Three cycles of full-matrix least squares refinement resulted in a conventional R value of 0.36. From an electron density map phased on these two atoms, the remaining non-hydrogen atoms were found. Several cycles of full-matrix least squares refinement

lowered the R value to 0.26. At this point the metal and iodide coordinates were damped to allow the coordinates to change by only 0.2 of the calculated amount. Further refinement then lowered the conventional R to 0.14. The weighting scheme of Ibers (14) was then introduced. Varying all of the coordinates, isotropic temperature factors, and the scale factor gave a conventional R1 of 0.13 and a weighted R2 of 0.09. Anisotropic temperature factors were applied to all of the atoms and after several more cycles of refinement, the R values were R1 = 0.065 and R2 = 0.11.

At this stage in the refinement a difference fourier was calculated and there appeared several peaks with a strength of more than one electron. A careful examination of the results showed that the nitrogens and oxygens might be disordered since the peaks in the difference fourier corresponded to possible positions for both the oxygens and the nitrogens. Since there were two possible positions for the oxygen and two possible positions for the nitrogen, it was decided to break the symmetry down to Pbca by removing the threefold axis. Absorption corrections were also made at this time since $\mu t = 1.97$ ($\mu = 39.48$ cm^{-1} and $t = 0.05$ cm)(23). Since the octahedral crystal was approximately equidimensional, absorption corrections were made assuming the crystal to be a sphere. After six cycles of refinement with isotropic temperature factors, the weighted R value came to 4.5 percent.

Since the percentage of occupancy for disordered nitrogen and oxygen sites was unknown, the site occupancies alone were varied. The results indicated that the Pa3 symmetry is well preserved and that the site occupancies of the alternate positions of nitrogens and oxygens were roughly

in the ratio of 1:1. Using the average coordinates and thermal parameters with Pa3 symmetry, the refinement yielded a weighted R of 6.85 percent. Anisotropic temperature factors were applied to the heavy atoms alone and isotropic temperature factors were applied to the light atoms. Further cycles of refinement yielded an R factor of 4.4 percent. The difference fourier calculated at this point showed no peaks greater than 0.5 $e^2/Å^3$. The final observed structural parameters are given in Table 1, and the calculated structure factors are given in Table 2.

Crystallographic Data for $Co_3(ETA)_6I_2 \cdot 6H_2O$

Good needle-like crystals were obtained from this preparation. A good single crystal was mounted along the long dimension of the crystal and precession camera photographs were taken using Mo Kα (λ = 0.7107 Å) radiation. These photographs indicated that the crystal was monoclinic with $a \neq b \neq c$ and $\beta \neq 90^\circ$. The systematic absences $h + k = 2n$ for the $hk\ell$ selection, $\ell = 2n$ for the h01 zone, and $k = 2n$ for the 0k0 zone indicated that the crystal was either C2/c or Cc (11). The calculated density of 2.05 g/cm^3 assuming four formula units per unit cell agreed well with the observed density of 2.02 ± .02 g/cm^3 measured by the flotation method using carbon tetrachloride and ethylene dibromide.

The crystal and goniometer head were then transferred to an automated Picker four-circle diffractometer and aligned. Six reflections were used to refine cell parameters and to determine angles for the other reflections. The cell parameters obtained were a = 22.3001(20) Å, b = 8.7950(10) Å, c = 15.0831(10) Å, and β = 88.790(5)°. Intensity measurements were made on the same crystal used for unit cell determination, and molybdenum radiation was again used. The procedure followed and the

Table 1. Positional and Thermal Parameters for $Ni(ETAH)_3Co(ETA)_3 \cdot I_2$

Atom	Mult.	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Metal	0.3333[a]	0.0987(5)[c]	0.0987	0.0987	0.0028	0.0028	0.0028	-0.0003	-0.0003	-0.0003
Iodide	0.3333[a]	0.2861(3)	0.2861	0.2861	0.0056	0.0056	0.0056	0.0008	0.0008	0.0008
C1	1.0000	-0.0105(12)	0.2262(14)	-0.0198(13)	4.51					
C2	1.0000	0.0570(11)	0.2941(15)	0.0378(13)	4.07					
O	0.6667[b]	0.0403(15)	0.1473(14)	-0.0338(16)	5.33					
O'	0.3333[b]	-0.0174(19)	0.1436(19)	0.0304(21)	1.18					
N	0.6667[b]	0.0541(17)	0.2452(18)	0.1374(19)	7.18					
N'	0.3333[b]	0.1507(24)	0.2327(28)	0.0501(25)	2.59					

[a] Fractional value due to special position.

[b] Fractional value due to disorder.

[c] Numbers in parentheses represent standard deviation in least significant figure(s).

Table 2. Observed and Calculated Structure Factors for $Ni(ETAH)_3Co(ETA)_3I_2$

L= 0

H	K	FO	FC
0	6	140	134
2	0	116	137
2	1	28	32
2	2	218	243
2	3	250	257
2	4	188	195
2	5	52	41
2	7	129	131
2	8	81	73
2	9	44	34
4	0	230	224
4	1	402	381
4	2	193	189
4	3	87	81
4	4	200	211
4	5	90	96
4	6	96	101
4	7	65	56
4	8	32	24
4	9	85	82
6	1	267	271
6	2	31	27
6	3	88	93
6	4	98	104
6	5	141	130
6	7	38	31
6	9	76	77
8	1	140	144
8	2	84	80
8	3	253	249
8	4	52	43
8	7	88	90

L= 1

H	K	FO	FC
1	2	158	160
1	3	13	19
1	5	102	91
1	8	101	94
1	9	56	51
2	2	169	185
2	3	120	116
2	4	196	194
2	5	21	15
2	6	194	197
2	7	141	135
2	8	195	189
2	9	105	98
3	2	61	66
3	3	51	62
3	4	125	111
3	5	53	59
3	6	135	128
3	8	60	52
4	2	141	136
4	3	115	119
4	4	101	104
4	5	225	234
4	6	105	101
4	7	147	142
4	8	160	161
4	9	83	85
5	3	40	45
5	4	29	14
5	5	91	90
5	7	80	82
5	9	74	68
6	2	50	50
6	3	150	150
6	4	81	84
6	5	215	210
6	6	66	67
6	7	151	149
6	9	91	91
7	2	109	112
7	4	54	56
7	5	97	100
7	6	38	32
7	7	44	41
7	8	64	68
8	2	37	33
8	3	133	131
8	5	86	87
8	6	25	24
8	7	141	139
8	8	49	45
8	9	121	127
9	2	62	61
9	4	34	35
9	5	78	70
9	8	38	41
9	9	22	25

L= 2

H	K	FO	FC
2	2	413	416
2	3	109	113
2	4	81	80
2	6	84	81
2	7	64	61
2	8	40	47
2	9	59	56
3	3	28	34
3	4	27	22
3	5	38	26
3	6	134	127
3	7	53	45
3	8	23	26
3	9	38	40
4	3	200	197
4	4	90	99
4	5	64	63
4	6	47	46
4	9	31	35
5	3	210	210
5	4	28	25
5	5	27	21
5	7	99	93
5	8	19	23
5	9	41	31
6	3	201	199
6	4	54	53
6	5	53	53
6	6	18	9
6	8	24	21
6	9	54	57
7	3	36	36
7	4	106	102
7	5	47	50
7	6	78	78
7	7	34	29
7	8	20	10
7	9	33	35
8	3	87	85
8	4	29	15
8	5	41	52
8	6	19	19
8	7	27	27
8	8	23	13
8	9	60	66
9	3	39	39

Table 2. (Continued)

H	K	FO	FC
9	4	70	70
9	5	19	14
9	6	35	35
9	7	47	46
9	9	42	49

L= 3

H	K	FO	FC
3	4	61	77
3	5	145	142
3	6	149	150
3	7	66	60
3	8	26	30
3	9	60	61
4	4	114	124
4	5	60	57
4	6	163	162
4	7	136	136
4	9	135	132
5	4	81	78
5	5	66	74
5	6	71	66
5	7	108	114
5	8	67	59
5	9	102	96
6	4	43	51
6	5	81	76
6	7	141	146
6	8	87	86
6	9	112	102
7	4	53	55
7	5	97	98
7	7	66	67
7	9	57	59
8	4	25	17
8	5	214	217
8	6	56	56
8	7	67	65
8	9	31	30
9	5	100	103
9	6	24	24
9	7	57	60
9	8	33	35
9	9	46	47

L= 4

H	K	FO	FC
4	4	39	29
5	8	31	28
4	5	49	44
4	6	56	55
4	7	86	86
5	5	87	85
5	6	16	16
5	7	63	59
5	9	68	73
6	5	64	63
6	6	73	68
6	7	35	32
6	8	28	25
7	2	16	2
7	5	55	50
7	6	24	26
7	8	19	26
7	9	25	18
8	6	24	16
8	9	48	48
9	5	60	56
9	6	36	32
9	7	38	35

L= 5

H	K	FO	FC
5	5	214	231
5	6	42	45
5	7	97	99
5	8	49	50
6	7	61	61
6	9	27	34
7	6	52	54
7	7	132	133
7	8	59	62
7	9	102	106
8	7	23	21
8	8	29	18
8	9	39	48
9	6	59	68
9	7	97	96
9	9	84	86

L= 6

H	K	FO	FC
1	1	14	6
3	6	18	15
6	6	44	49
6	7	42	41
6	9	47	47
7	7	27	24
7	8	20	13
7	9	25	36
8	7	70	63
9	7	26	29

L= 7

H	K	FO	FC
7	7	107	107
7	8	28	26
7	9	67	66
8	8	31	19
8	9	41	40
9	8	47	47
9	9	35	42

L= 8

H	K	FO	FC
4	4	18	17
8	3	18	7
8	9	21	16
9	9	58	56

L= 9

H	K	FO	FC
0	10	24	27
0	12	55	48
1	10	40	43
1	11	44	43
2	10	35	34
3	10	34	30
3	11	29	29
3	12	42	47
4	11	28	28
6	11	39	39
6	12	23	21
7	1	18	0
7	11	33	33
10	2	29	25
10	4	19	34
10	5	24	25
10	6	29	30
10	7	21	18
10	8	25	20
11	1	37	39

Table 2. (Continued)

H	K	FO	FC
11	2	43	40
11	3	34	34
11	4	27	27
11	6	27	25
11	7	33	38
12	1	25	22
12	5	44	44
12	6	22	15

L=10

H	K	FO	FC
0	0	153	140
0	2	59	57
0	4	17	17
0	6	91	88
0	10	85	96
1	0	130	127
1	1	27	25
1	2	89	85
1	3	25	27
1	4	59	57
1	8	19	16
1	10	45	40
1	12	31	38
2	0	69	63
2	2	89	87
2	3	129	127
2	4	87	81
2	7	47	46
2	12	29	26
3	0	84	84
3	1	73	65
3	2	81	81
3	3	61	56
3	4	54	55
3	5	30	30
3	9	25	20
3	10	34	23
3	11	29	25
3	12	28	30
4	1	92	86
4	2	79	73
4	4	93	91
4	5	40	38
4	6	27	27
4	7	35	39
4	10	22	23
4	11	29	32
4	12	26	30
5	0	48	42
5	1	81	85
5	2	22	13
5	3	54	47
5	5	18	22
6	0	97	86
6	1	99	100
6	3	25	26
6	4	24	28
6	5	27	16
6	6	40	45
6	10	48	47
6	11	27	36
7	1	85	87
7	3	62	64
7	5	43	42
8	1	25	17
8	3	82	89
8	5	30	32
8	7	54	55
9	4	22	17
11	0	55	52
11	1	27	31
11	2	33	30
11	4	24	23
12	1	52	48
12	2	37	32
12	3	26	25
12	4	28	27

L=11

H	K	FO	FC
0	4	99	93
0	6	98	109
0	8	34	33
1	3	41	36
1	4	78	77
1	5	47	42
1	6	74	74
1	7	41	44
1	11	29	25
2	3	29	33
2	4	37	40
2	6	61	59
2	7	36	45
2	8	55	56
3	1	47	46
3	2	92	94
3	3	33	23
3	5	25	27
3	7	21	22
3	8	62	71
4	3	42	42
4	4	33	32
4	5	69	74
4	6	30	28
4	7	31	33
4	8	63	65
4	11	33	30
5	1	43	40
5	3	19	18
5	4	23	14
5	5	97	100
5	7	33	30
6	3	29	28
6	5	70	70
6	6	22	18
6	7	56	60
7	1	43	43
7	2	47	47
7	3	31	27
7	4	19	19
7	5	34	35
7	6	21	24
7	7	42	44
7	8	47	42
8	1	37	39
8	3	44	47
8	7	45	49
10	5	34	33

L=12

H	K	FO	FC
0	0	96	94
0	2	97	106
0	4	72	77
0	8	20	17
1	0	60	56
1	2	37	34
1	3	61	63
1	7	38	37
2	1	47	49

Table 2. (Concluded)

H	K	FO	FC
2	2	84	76
2	4	38	35
2	5	26	21
2	6	23	24
3	0	32	39
3	2	50	56
3	3	25	32
3	4	51	55
3	6	46	41
3	7	26	17
3	8	31	18
4	0	86	86
4	1	57	67
4	2	46	41
4	3	58	62
4	5	33	34
4	6	24	24
5	1	16	10
5	3	25	22
5	7	38	45
6	1	55	52
6	2	28	28
6	3	70	73
6	4	22	20
6	5	29	18
7	0	40	39
7	3	32	37
7	4	44	42
7	6	29	34
7	7	25	16
8	0	21	27
8	1	74	75
8	3	30	29
8	5	27	23
8	7	20	19

L=13

H	K	FO	FC
0	2	80	89
0	4	27	27
0	6	27	30
0	8	92	97
1	6	23	20
2	1	30	38
2	4	61	63
2	5	79	82
2	6	71	76
2	8	35	40
3	1	19	13
3	2	20	13
3	5	23	15
4	1	38	41
4	2	29	28
4	3	41	45
4	4	66	64
4	6	61	54
4	7	48	51
5	3	26	19
5	5	21	18
6	1	42	39
6	2	48	45
6	3	48	47
6	5	24	21
6	7	48	56
7	2	21	12
8	1	23	25
8	3	23	20
8	5	80	82

L=14

H	K	FO	FC
0	0	51	36
0	2	59	62
0	4	80	82
0	6	21	18
0	8	22	14
1	0	25	11
1	3	28	41
1	6	27	23
1	7	22	16
2	0	67	79
2	1	52	55
2	2	64	59
2	4	20	19
2	6	20	16
2	7	29	26
3	0	29	37
3	2	19	19
4	1	36	35
4	3	63	60
4	6	25	26
5	1	28	22
5	3	22	24
5	4	20	3
6	2	24	19
6	3	57	57
6	4	28	27
6	5	22	17
7	0	38	33
8	0	27	19
8	1	60	61

L=15

H	K	FO	FC
0	4	49	46
0	6	42	48
1	1	42	40
1	2	27	21
1	5	34	34
2	2	29	28
2	3	21	21
2	4	36	34
3	2	48	50
4	2	23	17
4	3	23	21
4	4	26	25
5	1	30	31

L=16

H	K	FO	FC
0	0	88	84
1	0	41	44

programs used were the same as for the previous crystal.

A total of 1656 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.05 with P = 0.00. The intensities were corrected for Lorentz-polarization effects (15) but no corrections were made for absorption.

A three-dimensional Patterson synthesis (22) revealed possible positions for the iodide. A fourier calculation phased on this atom alone gave a conventional R value of 0.45. From the electron density map, positions were found for the cobalts and for the oxygens between them. The refinement stalled at this point and no further progress could be made. The corrected intensity data are listed in Table 3 for reference.

Magnetic Studies

The magnetic moments were all determined by the Faraday method and all measurements were made at room temperature. Corrections were applied to the gram susceptibilities to correct for the glass sample holder. Corrections for diamagnetism of the ligands and ions were made, using the diamagnetic corrections of Lewis and Wilkens (24), to obtain the molar susceptibilities. The magnetic moments were calculated from

$$\mu = 2.84 \ (\chi_m T)^{\frac{1}{2}}$$

where T is the absolute temperature. The results are tabulated in Table 4.

Spectral Studies

The visible spectra were recorded using a Cary model 14 spectrophotometer. The cells used were one-centimeter matched quartz. Samples were prepared just prior to being run, and in no case were the solutions

Table 3. Corrected Intensity Data for $Co_3(ETA)_6I_2 \cdot 6H_2O$

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
0		-14	27530	19	3	-13	4100	15	5	-12	2960	20	0	-10	15660
2	0	-14	14940	21	3	-13	3380	19	5	-12	3730	22	0	-10	3780
4	0	-14	11210	2	4	-13	3990	2	6	-12	2800	5	1	-10	18150
6	0	-14	4240	4	4	-13	3390	4	6	-12	2810	7	1	-10	19000
8	0	-14	13360	6	4	-13	3890	8	6	-12	4400	13	1	-10	20100
10	0	-14	7480	8	4	-13	8560	10	6	-12	3400	15	1	-10	4690
12	0	-14	10530	10	4	-13	6400	1	1	-11	44390	17	1	-10	3430
14	0	-14	14690	12	4	-13	4650	3	1	-11	44780	21	1	-10	3550
16	0	-14	4820	14	4	-13	4870	7	1	-11	16870	0	2	-10	8680
18	0	-14	7640	18	4	-13	2770	9	1	-11	17560	2	2	-10	25540
20	0	-14	4160	20	4	-13	2910	11	1	-11	3570	4	2	-10	33470
1	1	-14	3240	1	5	-13	3940	13	1	-11	17810	6	2	-10	17900
3	1	-14	5670	3	5	-13	3560	15	1	-11	7180	8	2	-10	50570
5	1	-14	9330	5	5	-13	9130	17	1	-11	3240	10	2	-10	56750
7	1	-14	3900	7	5	-13	4860	19	1	-11	9070	12	2	-10	5640
11	1	-14	5790	17	5	-13	2930	23	1	-11	3050	14	2	-10	6870
13	1	-14	3430	2	6	-13	8000	2	2	-11	6800	18	2	-10	3040
19	1	-14	3020	10	6	-13	7900	4	2	-11	20090	20	2	-10	9440
2	2	-14	4380	18	6	-13	2640	6	2	-11	3750	22	2	-10	6510
4	2	-14	10180	2	0	-12	16150	8	2	-11	7430	24	2	-10	3490
6	2	-14	5840	4	0	-12	7950	10	2	-11	6470	1	3	-10	23070
8	2	-14	9330	6	0	-12	9850	12	2	-11	3170	3	3	-10	18950
10	2	-14	11670	8	0	-12	18100	14	2	-11	4610	5	3	-10	4470
12	2	-14	4560	10	0	-12	59390	18	2	-11	2710	7	3	-10	3570
18	2	-14	10090	12	0	-12	10920	22	2	-11	3000	9	3	-10	7340
22	2	-14	2560	14	0	-12	3480	1	3	-11	6390	11	3	-10	14450
1	3	-14	10870	16	0	-12	3110	3	3	-11	55930	13	3	-10	11510
9	3	-14	11420	18	0	-12	7520	5	3	-11	23070	19	3	-10	3840
17	3	-14	3050	20	0	-12	3520	7	3	-11	12280	23	3	-10	3240
19	3	-14	2820	22	0	-12	7730	9	3	-11	6490	2	4	-10	3550
2	4	-14	6870	24	0	-12	4120	11	3	-11	6380	4	4	-10	11420
4	4	-14	3620	1	1	-12	16490	13	3	-11	5830	6	4	-10	11450
6	4	-14	3060	5	1	-12	7750	15	3	-11	5190	8	4	-10	9820
10	4	-14	2790	7	1	-12	10960	17	3	-11	5220	10	4	-10	10540
12	4	-14	2700	9	1	-12	7060	19	3	-11	8290	14	4	-10	3750
14	4	-14	3150	11	1	-12	12920	2	4	-11	23020	16	4	-10	3550
16	4	-14	3060	15	1	-12	4510	4	4	-11	8250	18	4	-10	3510
1	5	-14	6970	19	1	-12	2790	6	4	-11	5570	1	5	-10	7210
7	5	-14	2890	21	1	-12	2860	8	4	-11	7540	3	5	-10	14250
9	5	-14	6770	2	2	-12	8940	10	4	-11	14250	11	5	-10	11300
19	5	-14	3940	4	2	-12	18810	12	4	-11	15740	13	5	-10	11850
2	6	-14	3590	6	2	-12	8100	20	4	-11	6600	21	5	-10	3080
3	1	-13	19850	10	2	-12	7640	1	5	-11	8200	2	6	-10	12540
5	1	-13	14180	12	2	-12	21800	3	5	-11	13500	6	6	-10	5210
7	1	-13	4700	14	2	-12	9370	7	5	-11	5600	8	6	-10	3770
9	1	-13	23910	16	2	-12	6230	9	5	-11	3440	10	6	-10	2890
11	1	-13	6180	20	2	-12	6240	11	5	-11	7040	12	6	-10	3120
13	1	-13	3400	22	2	-12	2700	13	5	-11	6360	16	6	-10	2870
19	1	-13	14060	1	3	-12	7720	15	5	-11	5430	1	1	-9	42380
21	1	-13	2930	3	3	-12	15120	17	5	-11	2850	3	1	-9	143920
2	2	-13	9160	5	3	-12	5760	2	6	-11	5070	5	1	-9	21730
4	2	-13	5860	9	3	-12	3550	4	6	-11	7920	7	1	-9	16860
10	2	-13	9270	11	3	-12	11050	10	6	-11	7650	9	1	-9	22310
12	2	-13	4040	13	3	-12	4510	12	6	-11	7190	11	1	-9	29920
18	2	-13	2810	19	3	-12	4940	2	0	-10	5140	13	1	-9	46940
1	3	-13	8930	2	4	-12	4470	4	0	-10	177510	17	1	-9	6440
3	3	-13	6180	8	4	-12	4380	6	0	-10	23130	19	1	-9	6160
5	3	-13	4130	10	4	-12	10700	8	0	-10	20310	21	1	-9	4840
7	3	-13	7290	12	4	-12	5320	10	0	-10	17470	23	1	-9	8950
9	3	-13	20290	1	5	-12	15590	12	0	-10	27890	2	2	-9	21590
11	3	-13	3850	3	5	-12	9370	14	0	-10	17370	4	2	-9	38850
13	3	-13	5010	9	5	-12	7310	16	0	-10	15590	6	2	-9	5900
15	3	-13	3990	11	5	-12	5560	18	0	-10	10630	10	2	-9	13740

Table 3. (Continued)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
12	2	-9	16020	16	2	-8	23240	21	3	-7	11540	13	3	-6	3870
16	2	-9	3080	18	2	-8	15230	23	3	-7	7250	15	3	-6	27550
20	2	-9	4660	20	2	-8	7510	2	4	-7	3440	23	3	-6	5470
1	3	-9	45200	1	3	-8	12700	4	4	-7	89950	2	4	-6	26920
3	3	-9	10370	3	3	-8	28160	6	4	-7	5350	4	4	-6	21610
5	3	-9	16030	5	3	-8	58090	8	4	-7	10170	6	4	-6	5840
7	3	-9	5600	7	3	-8	5780	10	4	-7	31310	8	4	-6	26780
9	3	-9	8370	9	3	-8	8340	12	4	-7	17330	10	4	-6	26900
11	3	-9	27680	11	3	-8	5330	14	4	-7	9140	12	4	-6	13680
13	3	-9	36240	13	3	-8	32890	16	4	-7	7690	14	4	-6	13860
15	3	-9	7970	21	3	-8	4340	18	4	-7	4340	16	4	-6	4690
17	3	-9	3260	2	4	-8	14490	24	4	-7	7140	18	4	-6	6060
23	3	-9	4930	4	4	-8	33630	1	5	-7	25340	22	4	-6	3290
2	4	-9	33260	6	4	-8	8860	3	5	-7	28730	24	4	-6	2700
4	4	-9	23580	8	4	-8	8410	5	5	-7	8660	1	5	-6	14050
6	4	-9	9600	10	4	-8	5810	7	5	-7	3220	3	5	-6	7590
8	4	-9	11120	12	4	-8	8440	9	5	-7	9120	5	5	-6	28580
10	4	-9	4260	14	4	-8	15450	11	5	-7	10490	7	5	-6	8410
12	4	-9	7790	16	4	-8	6300	13	5	-7	10170	9	5	-6	5720
14	4	-9	28890	18	4	-8	4430	15	5	-7	6190	13	5	-6	8770
16	4	-9	2940	20	4	-8	4310	17	5	-7	7550	15	5	-6	21200
22	4	-9	6050	3	5	-8	6410	2	6	-7	8390	17	5	-6	3350
1	5	-9	5180	5	5	-8	18660	4	6	-7	12170	23	5	-6	4420
3	5	-9	19830	9	5	-8	5850	6	6	-7	12020	2	6	-6	21150
5	5	-9	12160	11	5	-8	3820	14	6	-7	19940	4	6	-6	4560
7	5	-9	21010	13	5	-8	15310	2	0	-6	244871	6	6	-6	18780
9	5	-9	9760	15	5	-8	6250	4	0	-6	437617	8	6	-6	5480
11	5	-9	6180	23	5	-8	3820	6	0	-6	240836	10	6	-6	5600
15	5	-9	3750	0	6	-8	3180	8	0	-6	89318	12	6	-6	4360
17	5	-9	4420	2	6	-8	6870	10	0	-6	19818	16	6	-6	10160
21	5	-9	3390	6	6	-8	7680	14	0	-6	165660	1	1	-5	75680
2	6	-9	4170	8	6	-8	3690	16	0	-6	12440	3	1	-5	61220
4	6	-9	14840	10	6	-8	7030	18	0	-6	25320	5	1	-5	436272
8	6	-9	3950	12	6	-8	8250	20	0	-6	24620	7	1	-5	88000
10	6	-9	3750	16	6	-8	3200	22	0	-6	3950	9	1	-5	79720
12	6	-9	9390	1	1	-7	63400	24	0	-6	9960	11	1	-5	19710
14	6	-9	4480	3	1	-7	4070	1	1	-6	99309	15	1	-5	70140
18	6	-9	3330	5	1	-7	301166	3	1	-6	41585	17	1	-5	36590
2	0	-8	71500	7	1	-7	47420	5	1	-6	162300	19	1	-5	22310
4	0	-8	177380	9	1	-7	81340	7	1	-6	18730	21	1	-5	3400
6	0	-8	86500	11	1	-7	28860	9	1	-6	17110	2	2	-5	57000
8	0	-8	65620	13	1	-7	50490	11	1	-6	20890	4	2	-5	139230
10	0	-8	97840	15	1	-7	37120	13	1	-6	15090	6	2	-5	19610
12	0	-8	27160	17	1	-7	9480	15	1	-6	3960	8	2	-5	67550
14	0	-8	100390	19	1	-7	21630	17	1	-6	10080	10	2	-5	41200
18	0	-8	20990	21	1	-7	4240	19	1	-6	8690	12	2	-5	5450
20	0	-8	6960	23	1	-7	15010	21	1	-6	3130	14	2	-5	6330
22	0	-8	5640	2	2	-7	32700	2	2	-6	25520	16	2	-5	31910
24	0	-8	11370	4	2	-7	26250	4	2	-6	78080	18	2	-5	5330
3	1	-8	52770	6	2	-7	55990	6	2	-6	29860	24	2	-5	4530
5	1	-8	9100	8	2	-7	8280	8	2	-6	71160	1	3	-5	140530
7	1	-8	20730	10	2	-7	5030	10	2	-6	95950	3	3	-5	112610
9	1	-8	41490	14	2	-7	35450	12	2	-6	77530	5	3	-5	132820
11	1	-8	23030	22	2	-7	4920	14	2	-6	79290	7	3	-5	10320
15	1	-8	12480	1	3	-7	4250	16	2	-6	39730	9	3	-5	4760
17	1	-8	8020	3	3	-7	9580	20	2	-6	32000	11	3	-5	11330
23	1	-8	3870	5	3	-7	93600	22	2	-6	30700	13	3	-5	18500
2	2	-8	48490	7	3	-7	79280	24	2	-6	16180	15	3	-5	75590
4	2	-8	241879	9	3	-7	73640	1	3	-6	52000	17	3	-5	8520
6	2	-8	13760	11	3	-7	8620	3	3	-6	38190	19	3	-5	4580
8	2	-8	10510	13	3	-7	5410	5	3	-6	67320	23	3	-5	3010
12	2	-8	5270	17	3	-7	10030	7	3	-6	63090	2	4	-5	37140
14	2	-8	54560	19	3	-7	8480	9	3	-6	29500	6	4	-5	125530

Table 3. (Continued)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
8	4	-5	5770	5	3	-4	74400	19	3	-3	8730	7	3	-2	116130
12	4	-5	6850	7	3	-4	32450	21	3	-3	7060	9	3	-2	124800
14	4	-5	42260	9	3	-4	26090	23	3	-3	7150	11	3	-2	7180
16	4	-5	3850	11	3	-4	26050	2	4	-3	24300	13	3	-2	11620
18	4	-5	3560	13	3	-4	3720	4	4	-3	14180	15	3	-2	7060
20	4	-5	2800	15	3	-4	15600	6	4	-3	49580	17	3	-2	10540
24	4	-5	6390	17	3	-4	10190	8	4	-3	124850	23	3	-2	2830
3	5	-5	8120	2	4	-4	41860	10	4	-3	23490	4	4	-2	108520
5	5	-5	35460	4	4	-4	13340	14	4	-3	9550	6	4	-2	57730
7	5	-5	27590	6	4	-4	22880	16	4	-3	13600	8	4	-2	39930
9	5	-5	14720	8	4	-4	64140	18	4	-3	7420	10	4	-2	5570
11	5	-5	22270	10	4	-4	24850	20	4	-3	4010	12	4	-2	14450
13	5	-5	7330	14	4	-4	8450	24	4	-3	3100	14	4	-2	13120
17	5	-5	3310	16	4	-4	12290	1	5	-3	58450	16	4	-2	21650
19	5	-5	5540	18	4	-4	5870	3	5	-3	85460	18	4	-2	11190
21	5	-5	5160	20	4	-4	4610	5	5	-3	16310	20	4	-2	4910
23	5	-5	3000	22	4	-4	4010	7	5	-3	15380	1	5	-2	13070
2	6	-5	14310	24	4	-4	4010	11	5	-3	15440	7	5	-2	32780
4	6	-5	14190	1	5	-4	3640	13	5	-3	17290	9	5	-2	52480
6	6	-5	9700	3	5	-4	4420	15	5	-3	19900	11	5	-2	3520
8	6	-5	11230	5	5	-4	59940	17	5	-3	5410	13	5	-2	5260
10	6	-5	9740	7	5	-4	30630	19	5	-3	5010	15	5	-2	4810
12	6	-5	3730	9	5	-4	8040	4	6	-3	9770	17	5	-2	14170
14	6	-5	5360	11	5	-4	6280	6	6	-3	32070	19	5	-2	6900
16	6	-5	11090	15	5	-4	15450	8	6	-3	10540	23	5	-2	2620
24	6	-5	3470	17	5	-4	10930	10	6	-3	5090	2	6	-2	17660
2	0	-4	40930	2	6	-4	10040	12	6	-3	4950	4	6	-2	23100
4	0	-4	59900	4	6	-4	9730	16	6	-3	9830	6	6	-2	18400
6	0	-4	30790	6	6	-4	21340	18	6	-3	7370	8	6	-2	19160
8	0	-4	119520	10	6	-4	10630	24	6	-3	2690	12	6	-2	4530
10	0	-4	112930	12	6	-4	18230	4	0	-2	1857309	14	6	-2	3420
12	0	-4	296886	16	6	-4	6050	6	0	-2	1510583	16	6	-2	7660
14	0	-4	60270	20	6	-4	3030	8	0	-2	184675	18	6	-2	4490
16	0	-4	103800	1	1	-3	230323	10	0	-2	87616	20	6	-2	3270
18	0	-4	15750	3	1	-3	109990	14	0	-2	17570	1	1	-1	745724
22	0	-4	11600	5	1	-3	188134	18	0	-2	15398	5	1	-1	177511
24	0	-4	21100	7	1	-3	15630	20	0	-2	18360	7	1	-1	230652
1	1	-4	261285	9	1	-3	51930	22	0	-2	8440	9	1	-1	287801
3	1	-4	22380	11	1	-3	47490	3	1	-2	194228	11	1	-1	28272
5	1	-4	95030	13	1	-3	31300	5	1	-2	151819	13	1	-1	20470
7	1	-4	62080	15	1	-3	102910	7	1	-2	117179	15	1	-1	13630
9	1	-4	29870	17	1	-3	10350	9	1	-2	36150	17	1	-1	15740
11	1	-4	38930	19	1	-3	16200	11	1	-2	37390	19	1	-1	46120
13	1	-4	12080	21	1	-3	4200	13	1	-2	32660	21	1	-1	8510
15	1	-4	19360	2	2	-3	148325	15	1	-2	15920	23	1	-1	5440
17	1	-4	9900	4	2	-3	24090	17	1	-2	5420	2	2	-1	69980
19	1	-4	3850	6	2	-3	173037	19	1	-2	9110	4	2	-1	141773
21	1	-4	4330	8	2	-3	95190	21	1	-2	4910	6	2	-1	51576
23	1	-4	3140	10	2	-3	22670	23	1	-2	3950	8	2	-1	106150
2	2	-4	178143	12	2	-3	28980	2	2	-2	343193	10	2	-1	149750
4	2	-4	147455	14	2	-3	18220	4	2	-2	96690	12	2	-1	20160
6	2	-4	295953	16	2	-3	19070	6	2	-2	69740	16	2	-1	9160
8	2	-4	206442	18	2	-3	4350	8	2	-2	190440	18	2	-1	21200
10	2	-4	26190	24	2	-3	3420	10	2	-2	50698	1	3	-1	113300
12	2	-4	4130	1	3	-3	8700	12	2	-2	49792	3	3	-1	248961
14	2	-4	35200	3	3	-3	45600	14	2	-2	59015	5	3	-1	188436
16	2	-4	11380	5	3	-3	138900	16	2	-2	63360	7	3	-1	106968
18	2	-4	40020	7	3	-3	4140	18	2	-2	15550	9	3	-1	126045
20	2	-4	18280	9	3	-3	184154	22	2	-2	4870	11	3	-1	26844
22	2	-4	5540	11	3	-3	93950	24	2	-2	6480	13	3	-1	28958
24	2	-4	5400	13	3	-3	3470	1	3	-2	8430	15	3	-1	30140
1	3	-4	21180	15	3	-3	16900	3	3	-2	53290	17	3	-1	13840
3	3	-4	19330	17	3	-3	6710	5	3	-2	4190	19	3	-1	20230

Table 3. (Continued)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
21	3	-1	5300	11	3	0	36240	2	4	1	119570	24	2	2	6420
2	4	-1	62281	13	3	0	5330	4	4	1	43470	1	3	2	146570
4	4	-1	47239	19	3	0	19390	6	4	1	7850	5	3	2	20723
6	4	-1	45510	0	4	0	29500	8	4	1	21140	7	3	2	29782
8	4	-1	106391	2	4	0	102340	10	4	1	140020	9	3	2	110701
10	4	-1	38346	4	4	0	104320	14	4	1	6150	11	3	2	40212
12	4	-1	14026	6	4	0	23230	16	4	1	3500	13	3	2	25362
14	4	-1	9010	8	4	0	6230	18	4	1	20430	15	3	2	9600
16	4	-1	19440	10	4	0	47870	20	4	1	4240	19	3	2	6220
18	4	-1	7290	12	4	0	22300	22	4	1	3940	21	3	2	6930
20	4	-1	7790	14	4	0	17270	24	4	1	4180	0	4	2	37020
22	4	-1	3090	16	4	0	11250	1	5	1	46820	2	4	2	25390
1	5	-1	13520	18	4	0	5490	3	5	1	89900	4	4	2	60240
3	5	-1	4580	22	4	0	3450	5	5	1	39960	6	4	2	24000
7	5	-1	43070	24	4	0	2850	7	5	1	42010	8	4	2	29630
9	5	-1	61660	1	5	0	37080	9	5	1	8660	10	4	2	45640
11	5	-1	28320	3	5	0	4560	11	5	1	5260	12	4	2	5930
13	5	-1	11610	5	5	0	17710	13	5	1	7090	14	4	2	6390
15	5	-1	4260	7	5	0	14770	15	5	1	14620	16	4	2	12770
21	5	-1	7740	9	5	0	58240	17	5	1	12490	18	4	2	3180
23	5	-1	5140	11	5	0	18690	19	5	1	4680	20	4	2	8290
2	6	-1	3950	15	5	0	3840	0	6	1	61100	22	4	2	4480
4	6	-1	8260	17	5	0	4540	2	6	1	5790	24	4	2	2970
6	6	-1	8900	19	5	0	18260	4	6	1	5050	1	5	2	115500
8	6	-1	17960	0	6	0	30430	6	6	1	5880	3	5	2	30370
10	6	-1	16040	2	6	0	23700	8	6	1	12620	5	5	2	7270
12	6	-1	3930	4	6	0	3810	10	6	1	7890	7	5	2	5130
14	6	-1	3130	8	6	0	12500	12	6	1	8070	9	5	2	15620
18	6	-1	15110	12	6	0	14080	14	6	1	5130	11	5	2	5860
6	0	0	101740	14	6	0	15380	16	6	1	3290	13	5	2	5460
8	0	0	141980	16	6	0	5420	18	6	1	4420	15	5	2	7790
14	0	0	219645	18	6	0	5780	20	6	1	10120	17	5	2	3020
16	0	0	43540	5	1	1	458560	4	0	2	332048	19	5	2	11480
18	0	0	14050	7	1	1	164610	6	0	2	1308397	21	5	2	4560
20	0	0	11200	9	1	1	175250	8	0	2	324829	2	6	2	22150
24	0	0	8210	11	1	1	83020	10	0	2	408795	6	6	2	33120
3	1	0	162881	13	1	1	25420	12	0	2	20367	8	6	2	19760
7	1	0	71520	15	1	1	62760	14	0	2	9490	10	6	2	6070
9	1	0	63000	17	1	1	19960	18	0	2	14600	12	6	2	9290
11	1	0	44050	19	1	1	50950	20	0	2	76070	18	6	2	4230
13	1	0	22320	0	2	1	110693	22	0	2	14060	22	6	2	4070
15	1	0	14760	2	2	1	93760	1	1	2	52427	1	1	3	1116406
17	1	0	25970	4	2	1	206360	3	1	2	190248	3	1	3	54080
21	1	0	6400	6	2	1	83600	5	1	2	247863	5	1	3	23630
23	1	0	3830	8	2	1	67050	7	1	2	93370	7	1	3	66370
0	2	0	555041	10	2	1	63790	9	1	2	15540	9	1	3	44500
2	2	0	186103	12	2	1	52730	11	1	2	105750	11	1	3	210121
4	2	0	830327	14	2	1	29220	13	1	2	7840	13	1	3	65959
6	2	0	152011	16	2	1	8130	15	1	2	7520	15	1	3	35326
8	2	0	20980	20	2	1	10450	17	1	2	15280	19	1	3	14570
10	2	0	376625	1	3	1	348079	19	1	2	16450	21	1	3	9040
12	2	0	16771	3	3	1	66490	23	1	2	3820	23	1	3	10160
14	2	0	22315	5	3	1	61710	0	2	2	1091984	0	2	3	123970
16	2	0	31200	7	3	1	127270	2	2	2	117320	2	2	3	332515
18	2	0	30190	9	3	1	143660	4	2	2	281103	4	2	3	44100
20	2	0	10860	11	3	1	40250	6	2	2	154640	6	2	3	33926
22	2	0	9820	13	3	1	41670	10	2	2	270535	8	2	3	42710
24	2	0	4320	15	3	1	12540	12	2	2	45318	10	2	3	89071
1	3	0	48050	17	3	1	7050	14	2	2	47898	14	2	3	5470
3	3	0	27680	19	3	1	14580	16	2	2	21950	16	2	3	13200
5	3	0	150250	21	3	1	7680	18	2	2	5530	18	2	3	8060
7	3	0	32850	23	3	1	4060	20	2	2	21420	20	2	3	5640
9	3	0	112660	0	4	1	104470	22	2	2	6350	22	2	3	6430

Table 3. (Continued)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
1	3	3	125820	0	2	4	11480	6	2	5	69980	11	1	6	26000
3	3	3	150350	2	2	4	90530	10	2	5	4350	13	1	6	20100
5	3	3	133570	4	2	4	207266	12	2	5	36910	15	1	6	3310
7	3	3	163150	6	2	4	228923	14	2	5	17900	19	1	6	9250
9	3	3	12800	8	2	4	50530	16	2	5	8890	21	1	6	3050
11	3	3	49010	10	2	4	84050	20	2	5	7450	23	1	6	3550
13	3	3	37210	12	2	4	48340	1	3	5	87340	0	2	6	148840
15	3	3	23670	14	2	4	21880	3	3	5	41650	2	2	6	204164
17	3	3	15510	16	2	4	4060	5	3	5	32410	4	2	6	135700
19	3	3	8920	18	2	4	10750	7	3	5	24240	6	2	6	42130
21	3	3	11780	20	2	4	29890	9	3	5	41690	8	2	6	16370
23	3	3	3200	24	2	4	3360	11	3	5	87820	10	2	6	6620
0	4	3	85350	1	3	4	16010	13	3	5	16500	12	2	6	10550
2	4	3	11380	3	3	4	126570	15	3	5	15360	14	2	6	79210
4	4	3	101190	5	3	4	29240	17	3	5	6110	16	2	6	15180
6	4	3	56740	7	3	4	4660	21	3	5	4420	18	2	6	8970
8	4	3	11840	9	3	4	4710	23	3	5	5820	20	2	6	3340
10	4	3	16800	11	3	4	60470	0	4	5	16920	22	2	6	3630
12	4	3	67260	13	3	4	20040	2	4	5	91900	24	2	6	2910
14	4	3	4880	19	3	4	6670	4	4	5	29250	1	3	6	26160
16	4	3	3530	21	3	4	6030	6	4	5	19110	3	3	6	16810
20	4	3	18890	0	4	4	27420	8	4	5	21780	5	3	6	48830
1	5	3	26410	2	4	4	45520	10	4	5	30070	9	3	6	13270
3	5	3	17500	4	4	4	60740	12	4	5	9780	11	3	6	9110
5	5	3	6980	6	4	4	45110	14	4	5	24080	13	3	6	16670
7	5	3	16620	8	4	4	18730	16	4	5	4050	15	3	6	7790
9	5	3	17600	10	4	4	18750	20	4	5	5360	21	3	6	3360
11	5	3	31720	12	4	4	13350	22	4	5	7950	23	3	6	4540
13	5	3	13200	14	4	4	13970	24	4	5	2980	0	4	6	38040
17	5	3	3270	16	4	4	14270	1	5	5	18310	2	4	6	31940
23	5	3	2760	18	4	4	3670	3	5	5	35170	4	4	6	91850
0	6	3	18880	20	4	4	5980	5	5	5	14980	8	4	6	15480
2	6	3	79520	1	5	4	28920	7	5	5	23640	10	4	6	4400
8	6	3	6220	3	5	4	79690	9	5	5	32210	12	4	6	13360
10	6	3	22240	11	5	4	23130	11	5	5	3430	14	4	6	10170
12	6	3	4050	13	5	4	7140	15	5	5	5380	16	4	6	8440
14	6	3	4200	19	5	4	5610	17	5	5	7090	1	5	6	4240
20	6	3	5500	21	5	4	5750	19	5	5	4060	3	5	6	25700
22	6	3	4060	23	5	4	4300	21	5	5	3090	5	5	6	71770
0		4	698298	0	6	4	5820	23	5	5	2780	9	5	6	5440
2	0	4	1588262	2	6	4	72820	2	6	5	26010	11	5	6	5100
4	0	4	442283	4	6	4	9850	4	6	5	79930	13	5	6	13140
6	0	4	66240	6	6	4	9170	12	6	5	7710	21	5	6	3660
8	0	4	9470	8	6	4	3990	14	6	5	5850	23	5	6	5060
10	0	4	132310	12	6	4	7670	16	6	5	3600	0	6	6	9640
12	0	4	8480	14	6	4	3590	20	6	5	2930	2	6	6	6510
14	0	4	103000	16	6	4	7980	22	6	5	4000	4	6	6	8880
16	0	4	87350	18	6	4	5050	0		6	127220	6	6	6	10530
18	0	4	13970	1	1	5	158310	2	0	6	71090	8	6	6	9350
20	0	4	15000	3	1	5	42770	4	0	6	192780	10	6	6	6680
22	0	4	13550	5	1	5	222040	6	0	6	60030	12	6	6	10060
1	1	4	336330	7	1	5	82450	8	0	6	106830	22	6	6	2670
3	1	4	61430	9	1	5	45960	10	0	6	86920	1	1	7	124450
5	1	4	135730	11	1	5	91460	12	0	6	132860	3	1	7	45040
7	1	4	63490	13	1	5	45000	14	0	6	19670	5	1	7	217380
9	1	4	44400	15	1	5	5790	18	0	6	10610	7	1	7	18900
11	1	4	4040	17	1	5	7140	20	0	6	14800	9	1	7	11210
13	1	4	48220	19	1	5	4140	22	0	6	3430	11	1	7	33150
15	1	4	8480	21	1	5	18240	24	0	6	15490	15	1	7	33260
17	1	4	11560	23	1	5	5440	3	1	6	65820	17	1	7	6760
19	1	4	3590	0	2	5	62070	5	1	6	29910	21	1	7	6690
21	1	4	5990	2	2	5	33130	7	1	6	49770	23	1	7	5120
23	1	4	3090	4	2	5	72650	9	1	6	25520	0	2	7	71090

Table 3. (Continued)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
2	2	7	29160	1	1	8	95550	4	2	9	31450	5	3	10	11110
4	2	7	23830	3	1	8	22150	6	2	9	35670	7	3	10	18810
6	2	7	33010	5	1	8	59440	8	2	9	7610	11	3	10	3710
8	2	7	29000	7	1	8	19020	10	2	9	6780	15	3	10	15640
10	2	7	13290	9	1	8	5000	12	2	9	8330	17	3	10	3480
12	2	7	14030	11	1	8	12030	14	2	9	13750	0	4	10	5110
14	2	7	8060	13	1	8	4560	18	2	9	4770	2	4	10	14310
16	2	7	4960	15	1	8	21340	1	3	9	47050	4	4	10	5300
18	2	7	4910	17	1	8	3390	3	3	9	29490	6	4	10	20420
20	2	7	2910	21	1	8	2750	5	3	9	3420	8	4	10	4030
24	2	7	3090	0	2	8	59510	7	3	9	9040	10	4	10	6260
1	3	7	7390	2	2	8	4270	9	3	9	6370	16	4	10	3310
3	3	7	16280	4	2	8	16230	11	3	9	6430	18	4	10	4070
5	3	7	74310	6	2	8	42380	13	3	9	12270	1	5	10	10420
7	3	7	54290	8	2	8	55210	15	3	9	29840	5	5	10	14950
9	3	7	24880	10	2	8	64100	0	4	9	16870	7	5	10	9810
11	3	7	5310	12	2	8	23310	2	4	9	14020	9	5	10	3350
13	3	7	10050	14	2	8	9610	4	4	9	12070	15	5	10	12790
15	3	7	7240	16	2	8	5990	6	4	9	19290	0	6	10	3500
17	3	7	9770	20	2	8	4040	8	4	9	19720	2	6	10	2960
19	3	7	6570	22	2	8	5990	10	4	9	10420	8	6	10	4430
21	3	7	7820	24	2	8	6390	12	4	9	4210	14	6	10	3280
0	4	7	15830	3	3	8	10440	14	4	9	6570	1	1	11	11270
2	4	7	5020	5	3	8	63490	16	4	9	15370	3	1	11	10590
4	4	7	87180	7	3	8	9310	24	4	9	3230	7	1	11	63910
6	4	7	31530	11	3	8	8780	1	5	9	4160	9	1	11	20790
8	4	7	11460	13	3	8	5380	3	5	9	11650	11	1	11	7000
10	4	7	4980	15	3	8	10170	5	5	9	14040	13	1	11	5960
12	4	7	6040	17	3	8	3520	7	5	9	6850	15	1	11	8860
14	4	7	24720	21	3	8	2710	9	5	9	9020	17	1	11	6140
16	4	7	3890	0	4	8	18320	11	5	9	4220	19	1	11	3310
20	4	7	4250	2	4	8	9970	17	5	9	4110	21	1	11	3190
22	4	7	3780	4	4	8	10920	0	6	9	5610	0	2	11	11540
1	5	7	12850	6	4	8	6940	4	6	9	3450	2	2	11	6740
3	5	7	17570	8	4	8	16600	6	6	9	14380	6	2	11	13940
5	5	7	24860	10	4	8	7600	8	6	9	6070	8	2	11	25090
7	5	7	8100	12	4	8	11660	14	6	9	6480	10	2	11	3200
9	5	7	12880	14	4	8	3170	0		10	63480	16	2	11	7880
11	5	7	7440	18	4	8	3030	2	0	10	43790	5	3	11	11130
13	5	7	11090	22	4	8	2600	4	0	10	5520	7	3	11	19380
15	5	7	4470	24	4	8	2670	6	0	10	105220	9	3	11	22200
17	5	7	3740	1	5	8	14210	8	0	10	80420	11	3	11	11970
0	6	7	9540	3	5	8	5850	10	0	10	27720	19	3	11	3280
2	6	7	6820	5	5	8	56170	12	0	10	17080	21	3	11	2830
4	6	7	21760	7	5	8	15910	16	0	10	20060	4	4	11	4620
6	6	7	13020	11	5	8	3950	18	0	10	3940	6	4	11	21820
10	6	7	3680	15	5	8	8930	20	0	10	9800	8	4	11	3010
12	6	7	3460	19	5	8	3650	24	0	10	3970	10	4	11	3380
14	6	7	9120	2	6	8	8510	5	1	10	9970	12	4	11	4580
24	6	7	3430	4	6	8	18380	7	1	10	29440	14	4	11	4190
0		8	181980	8	6	8	4810	9	1	10	9290	16	4	11	4360
2	0	8	87060	12	6	8	3670	11	1	10	14900	18	4	11	5840
4	0	8	16250	16	6	8	2690	13	1	10	5960	1	5	11	6700
6	0	8	262690	18	6	8	2880	17	1	10	5720	3	5	11	5460
8	0	8	13580	3	1	9	13780	2	2	10	34430	5	5	11	5020
10	0	8	11800	5	1	9	11579	4	2	10	21390	11	5	11	3180
12	0	8	7130	7	1	9	17330	6	2	10	105890	13	5	11	4050
14	0	8	57160	9	1	9	10360	14	2	10	3740	0	6	11	4560
16	0	8	13280	11	1	9	40700	16	2	10	17170	2	6	11	5770
18	0	8	15130	15	1	9	23550	18	2	10	9990	6	6	11	3830
20	0	8	8330	17	1	9	4240	20	2	10	3650	8	6	11	7130
22	0	8	5380	21	1	9	3360	1	3	10	7120	16	6	11	4600
24	0	8	8940	0	2	9	11540	3	3	10	4940	0		12	16390

Table 3. (Concluded)

H	K	L	INT	H	K	L	INT	H	K	L	INT	H	K	L	INT
2	0	12	28520	17	3	12	5010	12	2	13	3270	3	1	14	4360
4	0	12	27240	0	4	12	10050	18	2	13	3850	7	1	14	3190
6	0	12	50140	2	4	12	10410	1	3	13	7840	9	1	14	6880
8	0	12	8710	4	4	12	3980	3	3	13	12930	13	1	14	3050
10	0	12	10570	6	4	12	4020	5	3	13	6190	0	2	14	11440
16	0	12	14100	12	4	12	3870	7	3	13	6920	2	2	14	2880
18	0	12	3460	16	4	12	3590	15	3	13	2720	4	2	14	5050
3	1	12	9860	3	5	12	3100	17	3	13	6630	6	2	14	8020
5	1	12	6290	7	5	12	4290	0	4	13	23880	8	2	14	8970
7	1	12	20270	9	5	12	8400	8	4	13	9370	10	2	14	4950
13	1	12	5110	17	5	12	4100	14	4	13	3710	16	2	14	3140
15	1	12	4280	2	6	12	3490	16	4	13	5130	20	2	14	3100
0	2	12	41950	4	6	12	6170	5	5	13	3090	1	3	14	4640
2	2	12	9580	8	6	12	4180	7	5	13	3660	3	3	14	3270
6	2	12	16250	3	1	13	4320	9	5	13	4400	7	3	14	3200
8	2	12	5150	5	1	13	3640	0	6	13	6470	9	3	14	4520
10	2	12	14500	7	1	13	22020	4	6	13	5090	0	4	14	3050
12	2	12	9930	9	1	13	9670	10	6	13	4490	10	4	14	3800
14	2	12	3600	11	1	13	3940	18	6	13	2530	12	4	14	2740
16	2	12	5830	13	1	13	3630	2	0	14	8250	1	5	14	5670
18	2	12	3710	17	1	13	5020	10	0	14	19170	5	5	14	3370
5	3	12	5720	19	1	13	5480	12	0	14	5850	7	5	14	2820
7	3	12	3790	2	2	13	5000	16	0	14	3360	9	5	14	4510
9	3	12	10920	6	2	13	7950	18	0	14	6100	19	5	14	3000
11	3	12	3450	10	2	13	6050	1	1	14	8280	0	6	14	4230

Table 4. Magnetic Moment Data

Compound	$\chi_g \times 10^6$	$\chi_m \times 10^6$	μ(Bohr Magnetons)
$Co_3(ETA)_6I_2 \cdot 6H_2O$	--	--	4.91
$Ni(ETAH)_3\ Co(ETA)_3\ I_2$	5.188	4124	3.15
$NiCo_2(ETA)_6\ Br_2$	5.867	5100	3.50
$NiCo_2(ETA)_6\ I_2$	6.813	5716	3.70
$MgCo_2(ETA)_6\ I_2$	- .860	2.622	0.79
$Co\ (ETA)_3 \cdot 3H_2O$	-1.238	-1.601	0.00

more than one half hour old. To further insure that the complexes had not decomposed in solution, mull spectra were run to check on the bands. No meaningful absorption coefficients could be obtained from the latter spectra but the presence of the same bands indicated that no decomposition had taken place. The results are shown in Figures 6-11.

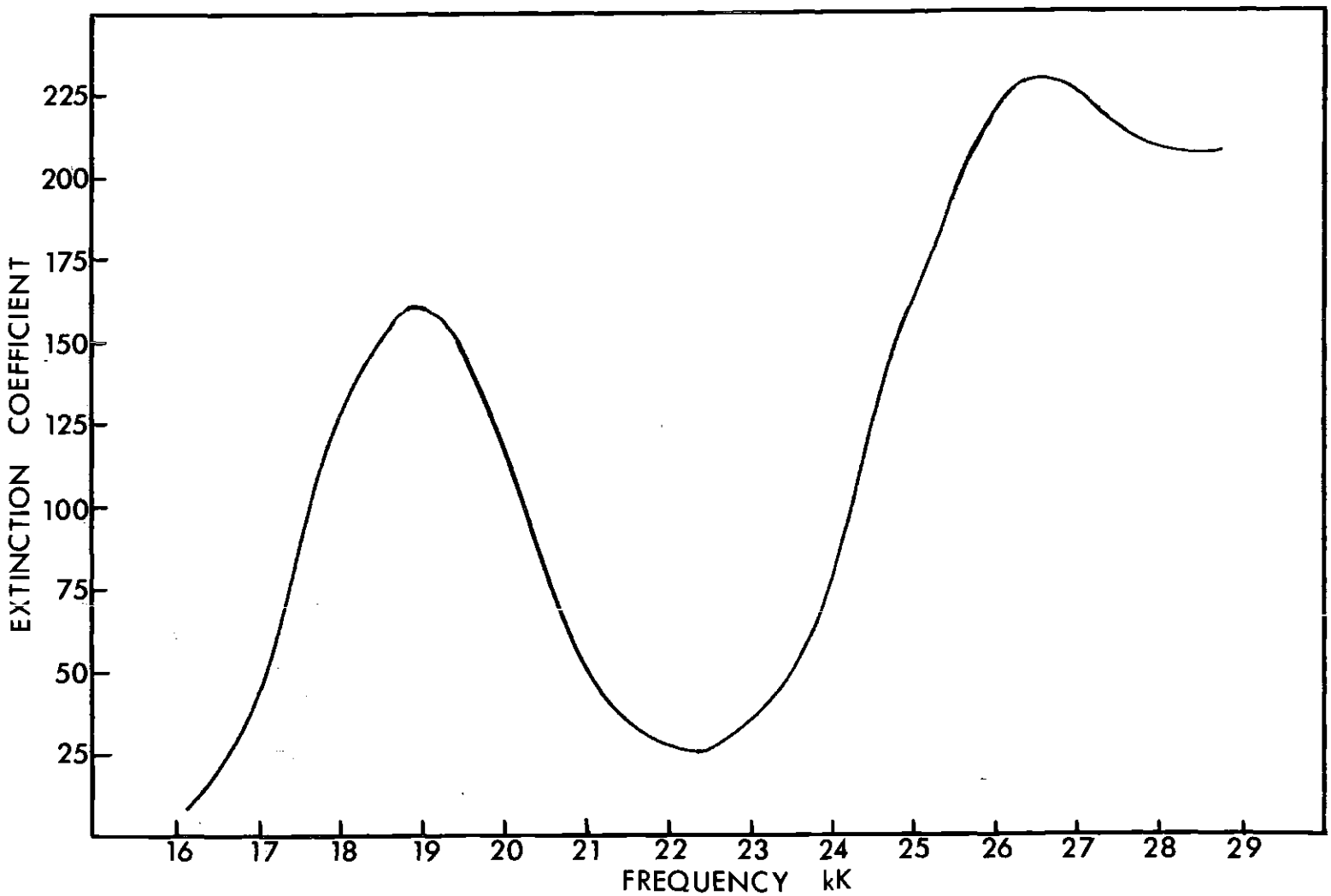

Figure 6. Solution Spectrum of $Ni(ETAH)_3Co(ETA)_3 I_2$ in Water

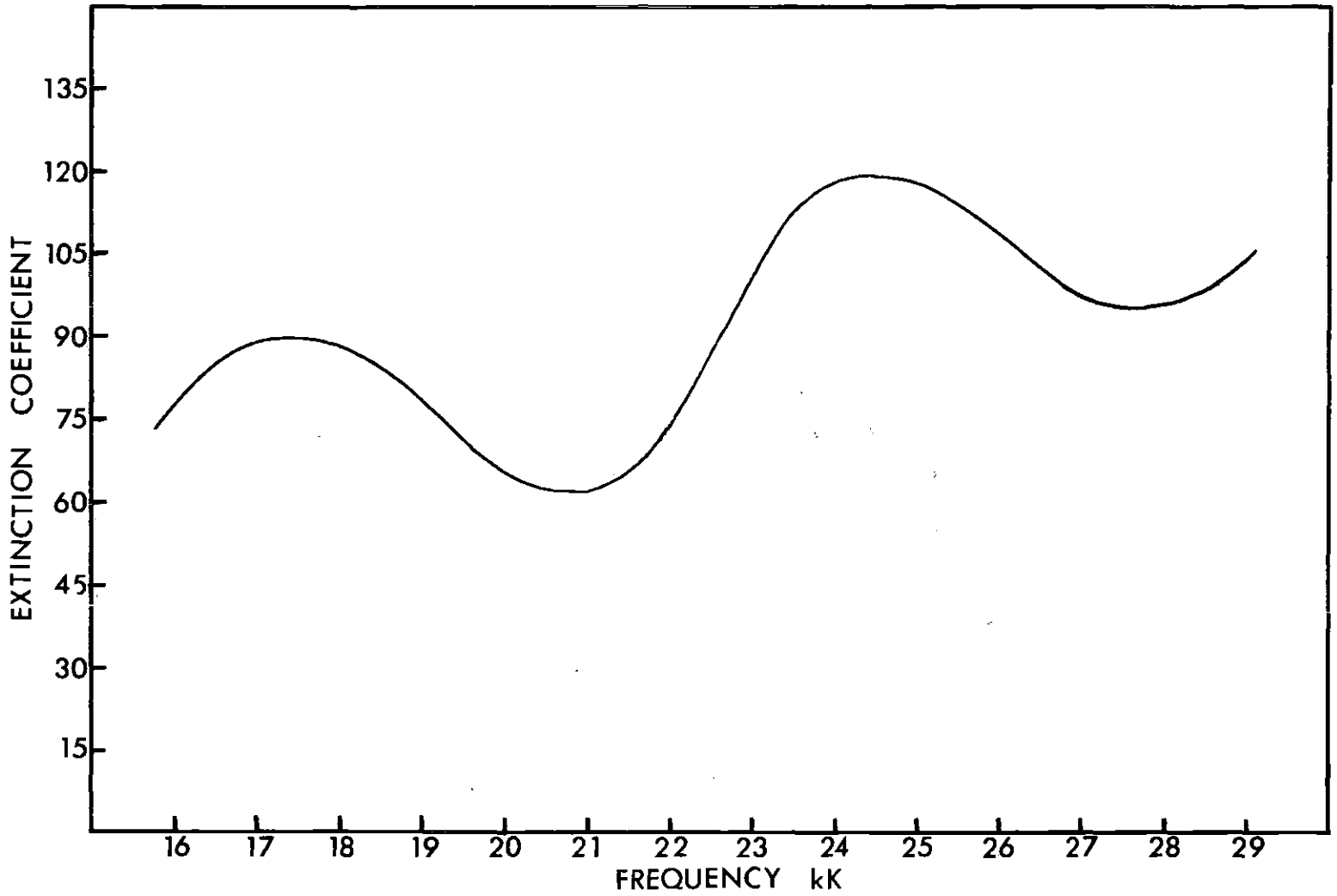

Figure 7. Solution Spectrum of $Co(ETA)_3 \cdot 3H_2O$ in Water

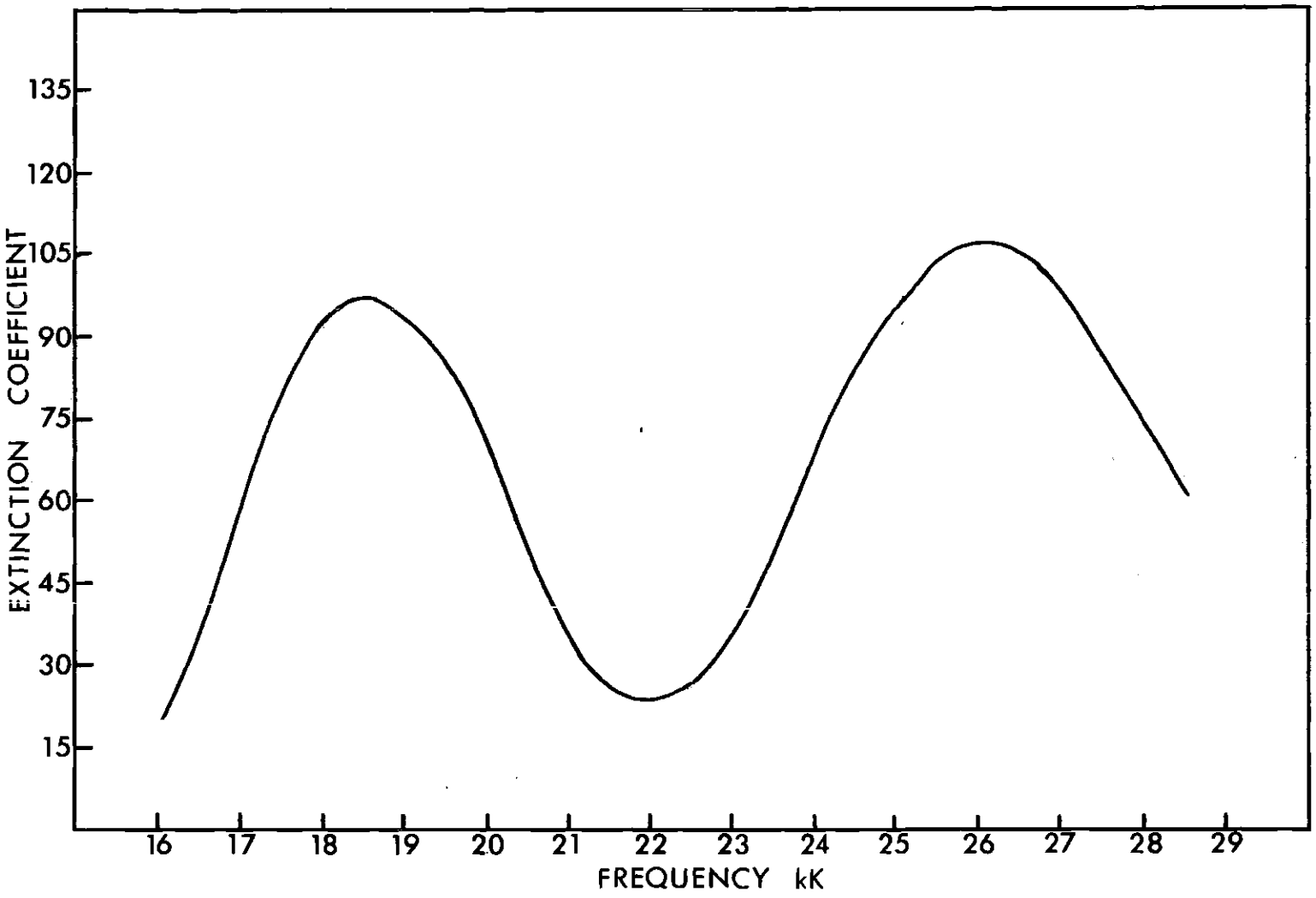

Figure 8. Solution Spectrum of $MgCo_2(ETA)_6I_2 \cdot 3H_2O$ in Water

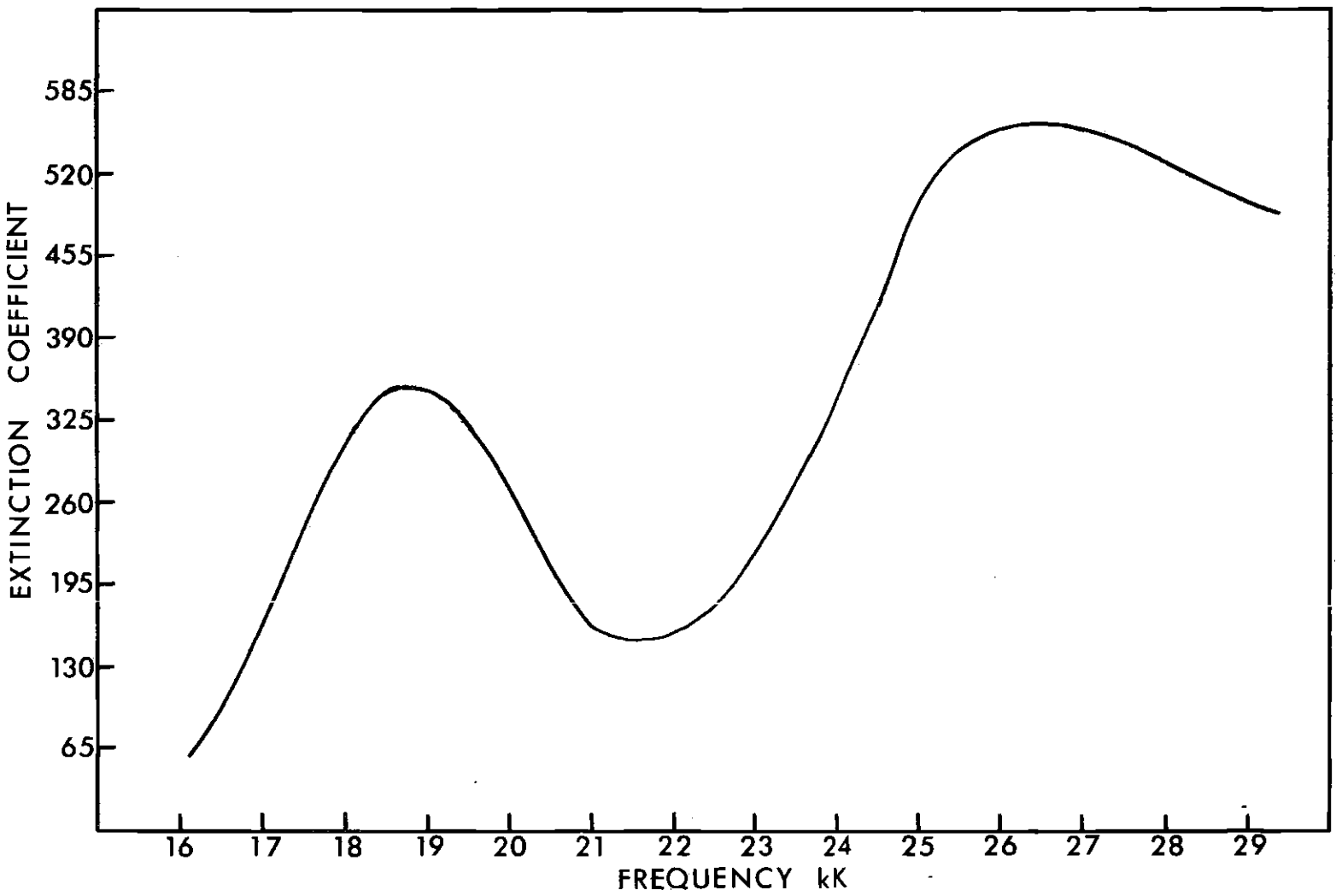

Figure 9. Solution Spectrum of $Co_3(ETA)_6I_2 \cdot 6H_2O$ in Water

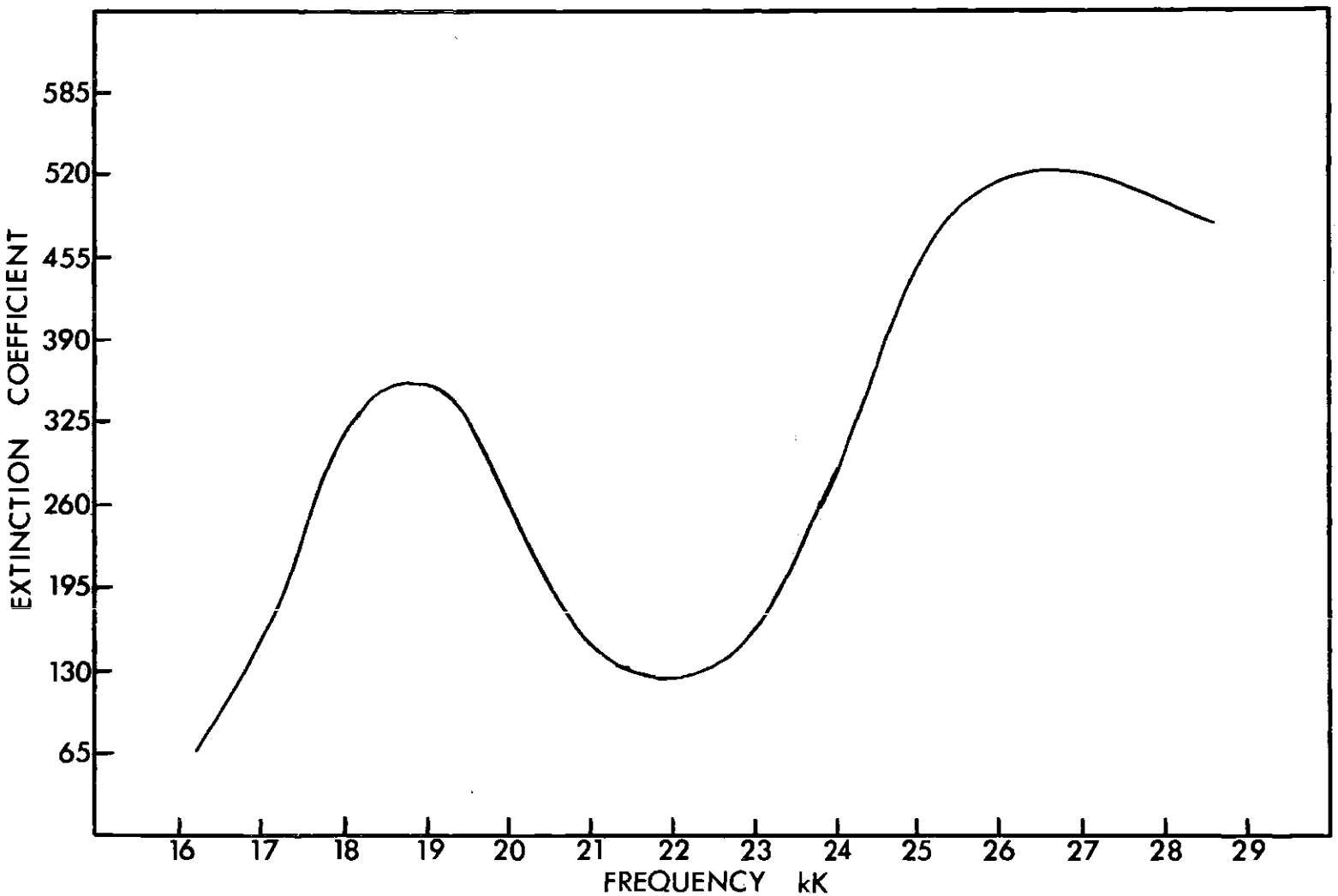

Figure 10. Solution Spectrum of $NiCo_2(ETA)_6I_2 \cdot 6H_2O$ in Water

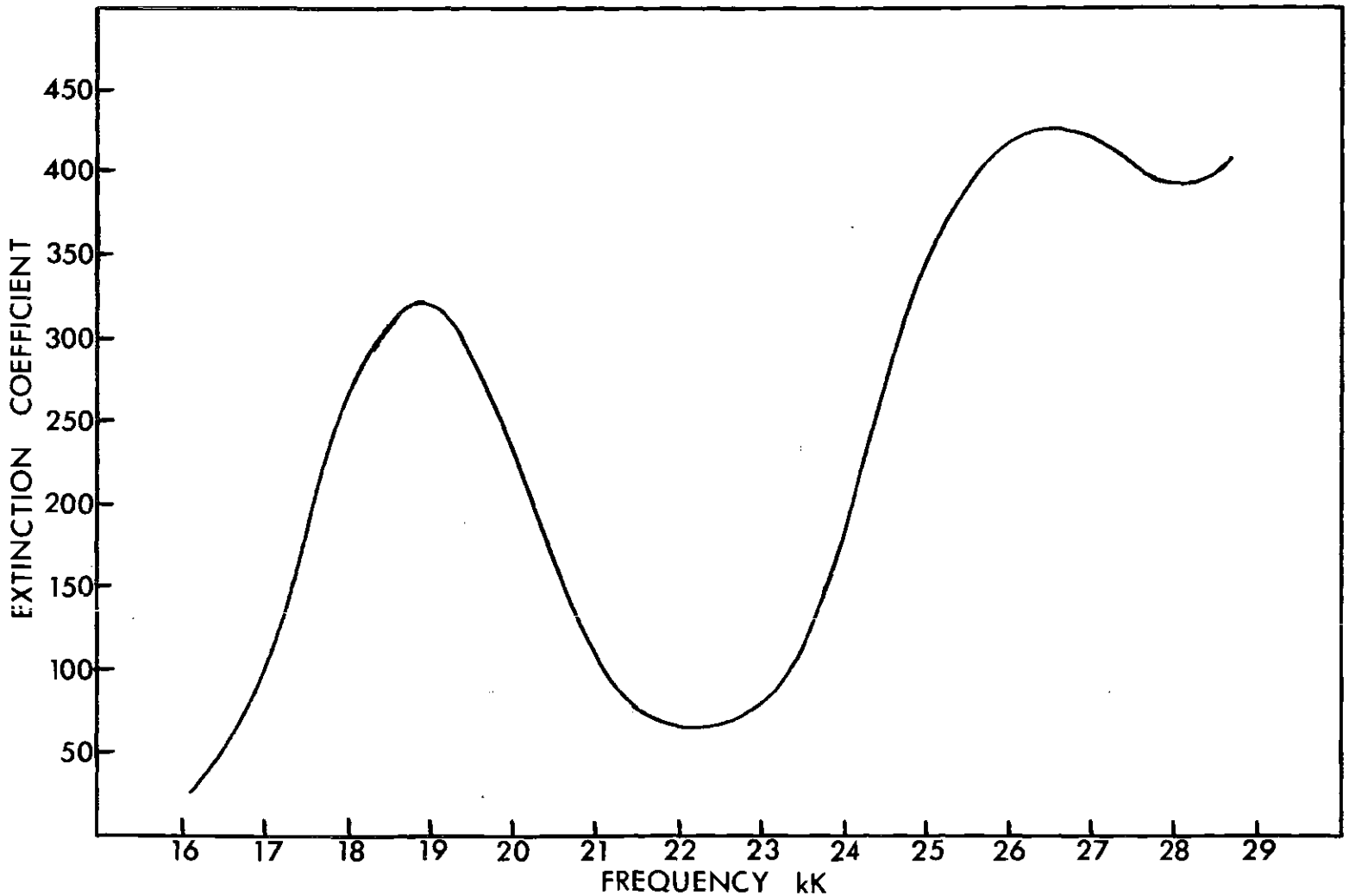

Figure 11. Solution Spectrum of $NiCo_2(ETA)_6Br_2 \cdot 6H_2O$ in Water

CHAPTER III

RESULTS AND DISCUSSION

Preparation of Complexes

The cobalt(III) tris-chelate of ethanolamine was prepared in good yield by reacting tris carbonato cobaltate(III) and ethanolamine with heating and stirring. The preparation gives a fairly good yield (~ 50 percent), and the product is relatively pure. This tris-chelate was reacted with several different metal ions in the ratio of two cobalt(III) tris-chelate to one metal ion. The compounds obtained were not always the expected trinuclear compound. Trinuclear compounds were prepared in this manner using magnesium(II), cobalt(II), and nickel(II). In addition, a dinuclear species of nickel(II) and cobalt(III) was obtained from the reaction of nickel(II) and the cobalt(III) tris-chelate. The mechanism for this reaction is not clear since all of the ethanolamine was chelated to cobalt(III) before the reaction took place.

The Structure of $(Ni)(Co)(ETA)_6I_2$

A perspective drawing of the structure is shown in Figure 12 and selected bond distances and bond angles are given in Table 5. The structure consists of an octahedrally coordinated tris-chelate of nickel and an octahedrally coordinated tris-chelate of cobalt joined together by face-to-face hydrogen bonding. The possibility of a structure of this type was discussed by Yoneda and Kida (4) for a dinuclear complex of cobalt(III).

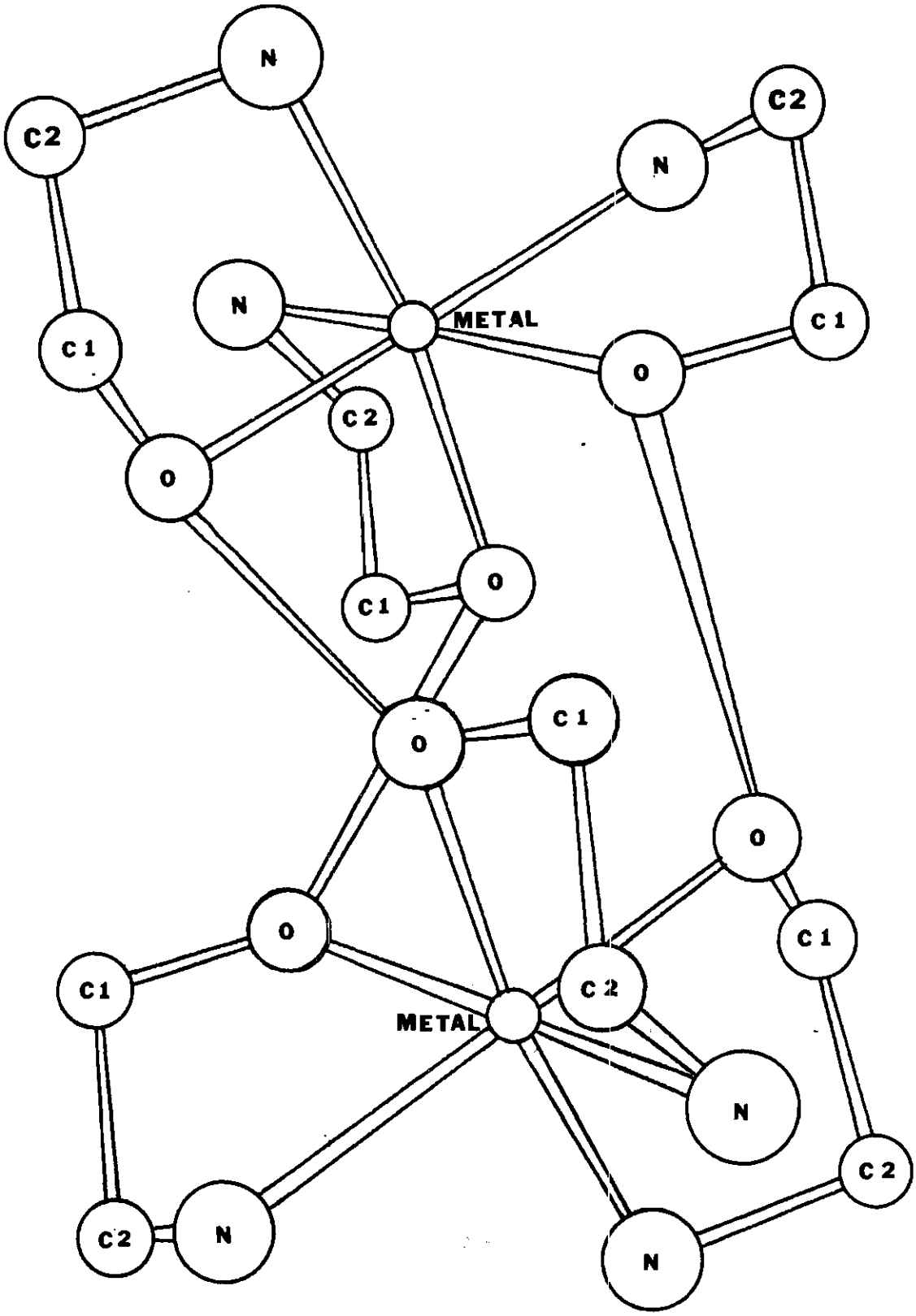

Figure 12. A Perspective Drawing of the Structure of $Ni(ETAH)_3Co(ETA)_3I_2$

Table 5. Bond Distances and Bond Angles for $Ni(ETAH)_3Co(ETA)_3I_2$

Atoms	Distance, Å	Atoms	Angle, Degrees
Metal-O	2.09(2)	Metal-O-C_1	107.1(1.6)
Metal-O'	1.92(2)	Metal-O'-C_1	119.8(1.8)
Metal-N	2.13(2)	Metal-N-C_2	102.5(1.5)
Metal-N'	2.07(3)	Metal-N'-C_2	102.7(1.6)
O-C_1	1.30(3)	O-C_1-C_2	107.6(1.6)
O'-C_1	1.25(3)	O'-C_1-C_2	106.0(1.7)
N-C_2	1.46(3)	C_1-C_2-N	100.9(1.5)
N'-C_2	1.53(3)	C_1-C_2-N'	101.7(1.7)
C_1-C_2	1.53(2)	O-Metal-N	80.0(0.8)
		O'-Metal-N'	74.5(0.9)

The metal atoms are located along the threefold axis of the unit cell on either side of the inversion center. The two different metal ions are completely disordered. The iodides are along the same threefold axis but they are located farther from the inversion center. The overall effect is to have both cations and anions along the threefold axis.

The distance between the two metal atoms is 4.66 Å. This compares to a distance of 5.19 Å between terminal cobalts in the trinuclear complex (9,25). The oxygen and nitrogen atoms of the ethanolamine ring are disordered but the carbon atoms are not. By taking this disorder into consideration and setting the site occupancy to 0.3333 for the nitrogen and 0.6667 for the oxygen, two disordered rings were determined. The

carbon-carbon bond distance is 1.53(2) Å for both of the units since the carbons are not disordered. The C-C-O and C-C-N bond angles are not significantly different in the two units with one set being 107.6(1.6)° and 100.9(1.5)° and the second set being 106.0(1.7)° and 101.7(1.7)°. The C-O and C-N bond distances are not very different from one unit to the other with values of 1.30(3) Å and 1.46(3) Å for one unit and for the second unit 1.25(3) Å and 1.53(3) Å.

Some very interesting differences are evident when the rest of the bond distances and angles are compared. For one unit the oxygen-metal and nitrogen-metal bond distances are 2.09(2) Å and 2.13(2) Å while for the other unit the distances are 1.92(2) Å and 2.03(3) Å. The angles are also different, the C-O-Metal, C-N-Metal, and O-Metal-N angles for one unit are 107.1(1.6)°, 102.5(1.5)°, and 80.0(0.8)° while for the second unit the angles are 119.8(1.8)°, 102.7(1.6)°, and 79.5(0.9)°.

The M-O and M-N bond distances and the M-O-C and M-N-C bond angles may be compared to those found in the trinuclear complex $Co_3(ETA)_6^{2+}$. In the trinuclear complex the average Co(III)-O bond distance was 1.93 Å while the average Co(III)-N bond distance was 1.99 Å. The average Co-(III)-O-C angle was 118.0° and the average Co(III)-N-C angle was 109.0°. The conclusion to which these results seems to point is that there is indeed one nickel(II) and one cobalt(III) present in each dimeric unit since in one case the bond distances and bond angles are very similar to those in the trinuclear cobalt compound while in the second unit the bond distances and bond angles are somewhat different.

The oxygen-oxygen distances between tris-chelate octahedra are

2.5 Å. This means that the hydrogen bonds formed here are strong since the shortest O-O hydrogen bond distance previously reported (26) of any compound is 2.38 Å (an unpublished value of 2.31 Å has been obtained in these laboratories).

There are other difficulties which are related to the high symmetry. It is impossible to tell from the X-ray work if one actually has a dinuclear species which contains one nickel and one cobalt per dimer or a mixture of Ni-Co, Ni-Ni, and Co-Co dimers. The X-ray work does give an indication from the bond distances and bond angles that there is one nickel and one cobalt per dimer but this cannot be proven conclusively. The magnetic moment of the dinuclear species, 3.15 Bohr Magnetons, tells nothing about the structure and the visible spectrum is not helpful in this respect.

The Partial Structure of $Co_3(ETA)_6I_2 \cdot 6H_2O$

Although refinement of this structure was not completed, some general characteristics of the structure can be given. The only positions found were the cobalts and the shared oxygens. The coordination of the central cobalt(II) ion appears to be trigonal prismatic from the limited results. From this preliminary work nothing can be said about the isomeric forms of the complex except that, based on symmetry arguments, the complex is probably composed of two active forms of the same type of tris-chelate, either d-d or l-l.

Further work should be done towards separating the different isomers as discussed earlier. A separation should be possible but it might be necessary to use a larger anion then iodide. The size effect of a larger anion might lock the structure more securely and allow only one form of the complex. A separation could then be made more easily. It

would also be better to obtain a complex with no water molecules present; the water molecules in the iodide complex prepared in this work are probably disordered thus adding to the difficulty in solving the structure.

Another very interesting aspect of the trinuclear complexes that should be investigated further is that of the heteronuclear complexes. Several of these complexes were prepared in this work. If structures of these compounds could be determined, some very interesting results should be obtained. Comparison of the heteronuclear complex and complexes containing only one type of metal ion should also be very interesting.

Magnetic Studies

Magnetic moments were particularly useful in establishing the identity of metal ions and their oxidation states in two of the compounds studied. As was indicated earlier, the oxidation state of the cobalt in the cobalt tris-chelate of ethanolamine was initially believed to be 2+ but later work showed that the oxidation state was 3+. In the work of Yoneda and Kida (4), the oxidation state was established from spectral comparisons; in the work of Udovenko (5) the oxidation state was established by separate analyses for cobalt(II) and total cobalt. Since the tris-chelate prepared in this work was obtained by a new procedure, it was desirable to confirm the 3+ oxidation state. An effective way of doing this was through the magnetic moment. The experimental results, which showed that the compound was diamagnetic at all field strengths was consistent with a compound containing only cobalt(III).

The compound formed from magnesium ion and the cobalt(III) tris-

chelate also gave interesting magnetic results. Since both magnesium-(II) and cobalt(III) are diamagnetic, the compound was expected to be diamagnetic. All preparations, however, were paramagnetic; apparently some of the cobalt(III) was reduced to cobalt(II) and the magnesium(II) complex was contaminated with the corresponding cobalt(II) complex. The lowest moments obtained were in the range of 0.7 to 0.8 Bohr Magnetons. Based on a moment of 4.9 B.M. for the trinuclear complex containing cobalt(II), the percent of magnesium replaced by cobalt(II) was calculated to be about two percent.

Magnetic moments obtained for the complexes with paramagnetic metal ions are within the range normally found for these metal ions.

Spectral Studies

Cobalt(III) complexes are normally spin-paired octahedral complexes and show two absorptions in the visible region. One transition corresponds to the transition from the ^1A_1g ground state to the ^1T_1g state and the other corresponds to the transition from the ^1A_1g state to the ^1T_2g state; these bands are generally found at about 20 Kk and 28 Kk, respectively. In this work all of the complexes gave two peaks in the visible region but the peak at about 28 Kk was partially obscured by a very strong absorption in the UV region.

The spectra here in all cases are most like those obtained by Yoneda and Kida (4) for the tris-chelate of cobalt(III). In the work of Yoneda and Kida the two bands are at the same relative positions (20 and 28 Kk) and are about the same intensity as those obtained here. The bands are both nearly symmetric and no splitting is observed in any of the spectra.

The spectrum of the tris-chelate does show very broad bands and it was, therefore, harder to assign a value to the transition.

The possibility of geometric isomers as reported by Udovenko (8) should be evidenced by a non-symmetric absorption due to splitting of the absorption bands. In the work of Udovenko no split was observed but a much broader and less intense band resulted for the cis-trans type of isomer. None of the spectra obtained in this work shows any splitting and all are relatively symmetric. The only questionable spectrum is that of the cobalt(III) tris-chelate which does exhibit somewhat broader bands than the other spectra, but there is no real evidence for isomers.

The spectrum of the magnesium compound was very similar to the others except that the extinction coefficients were lower than for the complex containing cobalt(II). Subtraction of the spectrum of the magnesium trinuclear compound from that of the cobalt(II) trinuclear compound did not reveal any additional transitions that could be assigned to the cobalt(II); no bands due to the nickel(II) ions could be identified in the spectra of the dinuclear and trinuclear complexes of nickel(II). It appears that the extinction coefficients of these ions are too low to be observed in the presence of the strong bands of the cobalt(III) complexes.

CHAPTER IV

CONCLUSIONS

A new preparation of the ethanolamine tris-chelate of cobalt(III) is reported; the preparation employs a standard starting material, the cobalt(III) carbonato complex, and the product is obtained in good yield. There is less chance of contamination of the product with cobalt(II) (as the trinuclear complex) or chloride (as the salt of the dinuclear cation).

The tris-chelate has been used to prepare trinuclear complexes in which the tris-chelate serves as a ligand; trinuclear complexes of cobalt-(II), magnesium(II), and nickel(II) have been prepared.

The trinuclear complex of cobalt(II), Co $(Co(ETA)_3)_2I_2 \cdot 6H_2O$ was investigated by X-ray diffraction to determine whether the trinuclear compound contained the isomer previously reported (9) or a different isomer. Although the refinement of the X-ray data did not progress satisfactorily, the results indicated trigonal-prismatic coordination of the cobalt(II).

A dinuclear compound containing nickel(II) and cobalt(III) tris-chelates has been prepared although the mechanism of the formation is not clear, since there was no excess ethanolamine, the groups chelating nickel(II) were originally bound to cobalt(III).

The crystal structure of the dinuclear compound has been determined.

The cation consists of the two tris-chelates joined by very strong face-to-face hydrogen bonding similar to a structure proposed by Yoneda and Kida (4) for a dinuclear complex of cobalt(III) shown in Figure 3. The bond distances and angles are very similar to those in the trinuclear complex which has been reported (9). The latter suggestion by Udovenko of a structure involving mono state and chelate ethanolamine groups for the cobalt(III) dinuclear compound is probably wrong. Based on the present results for the nickel-cobalt dinuclear compound, a hydrogen bonded structure is likely for the cobalt(III) compounds and for a similar series of chromium(III) compounds reported by Udovenko (27).

Magnetic properties have been used in conjunction with other analyses to determine the identity of the cobalt(III) tris-chelate and the magnesium(III) trinuclear complex. Magnetic properties for the other compounds revealed little about their identity and all were in the normal range for the ions under study.

The spectra obtained for all of the compounds exhibit essentially the same peak positions and the same range of extinction coefficients. They all compare very well with previous results and there is no real indication of the presence of any species other than the cis-cis type of geometric isomer. From this work it appears that the major spectral contribution is from the cobalt(III) tris-chelate and that this masks any other transitions present.

REFERENCES

1. W. Hieber and E. Levy, Annalen, 500, 14 (1932).

2. W. Hieber and E. Levy, Z. Anorg. Chem., 219, 225 (1934).

3. H. Brintzinger and B. Hesse, Z. Anorg. Chem., 248, 345 (1941).

4. H. Yoneda and S. Kida, J. Amer. Chem. Soc., 82, 2139 (1960).

5. V. V. Udovenko and A. N. Gerasenkova, Russ. Jour. Inorg. Chem., 11, 1105 (1966).

6. V. V. Udovenko and A. N. Gerasenkova, Russ. Jour. Inorg. Chem., 12, 654 (1967).

7. G. R. Brubaker and B. E. Douglas, Inorg. Chem., 6, 1562 (1967).

8. V. V. Udovenko and O. I. Stepanenko, Russ. Jour. Inorg. Chem., 14, 827 (1969).

9. J. A. Bertrand, J. A. Kelley, and E. G. Vassian, J. Amer. Chem. Soc., 91, 2394 (1969).

10. D. H. Busch and D. C. Jicha, Inorg. Chem., 1, 884 (1962).

11. "International Tables for X-Ray Crystallography," 1965, The Kynock Press (Birmingham, England), Vol. I.

12. "Full Circle Goniostat Alignment," Picker Instruments, Cleveland, Ohio (1968).

13. F. Carter, "Master Card Program for the Picker Four-Angle Programmer," Picker Instruments, Cleveland, Ohio (1967).

14. P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, Inorg. Chem., 6 (1967).

15. D. A. Carpenter, Ph.D. Dissertation, Georgia Institute of Technology, 1968, p. 61.

REFERENCES (Concluded)

16. A. Zalkin, Fortran Fourier Analysis Program, FORDAP, 1962.

17. L. J. Gallaher and M. I. Kay, "A Translation of a Fortran Crystallographic Least Squares Program by W. R. Busing, K. O. Martin, and H. A. Levy to Extended Algol," Georgia Institute of Technology, Technical Report No. 1, Project B-270, May 27, 1964.

18. W. R. Busing, K. O. Martin, and H. A. Levy, "Fortran Crystallographic Least Squares Program, XFLS (modified version of ORFLS), Oak Ridge National Laboratories, 1963.

19. W. R. Busing, K. O. Martin, and H. A. Levy, "Fortran Function and Error Program," ORFFE, Oak Ridge National Laboratories (1965).

20. C. E. Kirkwood, "Fortran Program for Reduction of Diffractometer Data" (1967).

21. "International Tables for X-Ray Crystallography," 1965, The Kynock Press (Birmingham, England), Vol. III.

22. M. J. Buerger, "Crystal-Structure Analysis," John Wiley and Sons, New York, 1960.

23. "International Tables for X-Ray Crystallography," 1965, The Kynock Press (Birmingham, England), Vol. III.

24. B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkens, ed., Interscience Publishers, Inc., New York, 1960, p. 403.

25. J. A. Kelley, Ph.D. Dissertation, Georgia Institute of Technology, 1969.

26. E. O. Schlemper, Inorg. Chem., 7, 1130 (1968).

27. V. V. Udovenko and O. N. Stepanenko, Russ. Jour. Inorg. Chem., 14, 91 (1969).